Corrosion

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TECHNICAL SECTION

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SCHEDULED FOR PUBLICATION IN DECEMBER

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Plastic Flow of Iron Oxides and the Oxidation of Iron by J. D. Mackenzie.

The Use of Aluminum Alloys With Short Chain Aliphatic Acids and Anhydrides by A. E. McKee and W. W. Binger.

Polarization in the Corrosion of Ice Breakers by J. H. Greenblatt.

Inhibiting Effect of Hydrofluoric Acid in Fuming Nitric Acid on Liquid—And Gas-Phase Corrosion of Several Metals by David M. Mason, Lois L. Taylor and John B. Rittenhouse.

Corrosion Research Being Carried Out in the Department of Chemistry at the University of Virginia by A. T. Gwathmey.

Section III of the T-3B Bibliography of Corrosion Products—Bibliography on Identification of Corrosion Products of Nickel and Nickel Alloys, 1943—Jan. 1956 Inco Library through W. Z. Friend, International Nickel Co.

Corrosion and Metal Transport in Fused Sodium Hydroxide. III. Formation of Composite Scales on Inconel by G. Pedro Smith, Mark E. Steidlitz and Eugene E. Hoffman.

TECHNICAL TOPICS

Urethane Coatings, Structure, Characteristics and Uses by Richard C. Burck.

Some Keys to Successful Industrial Contract Painting by L. L. Sline.

Spray Injection of Liquids into High Pressure Gas Line by F. E. Blount and J. W. Anthony.

THIS MONTH'S COVER—Shown here is a stainless steel hollow axle and a part of a stainless steel vane removed from a carbon black plant. The hollow axle is perforated by Corrosion near the cap (upper end) and the vane segment is badly pitted and eroded. The dark colored fittings shown with pipe nipples are believed to be wrought iron and are substantially undamaged. No further information is available. It illustrates truism corrosion can be found in any plant and that materials selection is not easy.

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Jack L. Battle, Chairman; Humble Oil & Refining Co., P. O. Box 2180, Houston, Texas

W. C. Koger, Vice Chairman; Cities Service Oil Co., Cities Service Bldg., Bartlesville, Okla.

T-1A Corrosion in Oil and Gas Well Equipment, Los Angeles Area
H. J. Kipps, Chairman; Signal Oil & Gas Company, 2780 Junipero Ave., Long Beach 6, Cal.
L. W. Brock, Vice Chairman; Long Beach Harbor Dept., 1333 El Embarcadero, Long Beach, Cal.

T-1B Condensate Well Corrosion
W. H. Edwards, Chairman; Superior Oil Company, 400 Oil & Gas Bldg., Houston, Texas
D. R. Fincher, vice-chairman; Tidewater Oil Co., 1538 Campbell Road, Houston 24, Texas

T-1B-1 High Pressure Well Completion and Corrosion Mitigation Procedure
W. F. Oxford, Jr., Chairman; Sun Oil Co., Box 2831, Beaumont, Texas

T-1C Sweet Oil Well Corrosion
Joy T. Payton, Chairman; The Texas Co., Box 2332, Houston, Texas
Rado Loncaric, Vice Chairman; Atlantic Refining Co., Box 2819, Dallas, Texas

T-1C-1 Water Dependent Corrosion, Field Practices
Joy T. Payton, Chairman; The Texas Co., Box 2332, Houston, Texas

T-1C-2 Water Dependent Corrosion, Experimental Aspects
J. A. Rowe, Chairman; Gulf Oil Corp., Drawer 2100, Houston, Texas

T-1C-3 Water Independent Corrosion, Field Practices
H. E. Greenwell, Chairman; Production Profits, Inc., 8912 Sovereign Row, Dallas, Texas

T-1C-4 Water Independent Corrosion, Experimental Aspects
Rado Loncaric, Chairman; Atlantic Refining Co., Box 2819, Dallas, Texas

T-1C-5 East Texas Task Group
H. G. Byars, Chairman, 6405 Bordeaux, Dallas, Texas

T-1D Sour Oil Well Corrosion
R. E. Lembcke, Chairman; Cities Service Research & Development Co., 920 East Third Street, Tulsa, Okla.
J. V. Gannon, Vice Chairman; The Texas Co., Box 1270, Midland, Texas

T-1D-1 Fundamentals of Corrosion
J. D. Sudbury, Chairman; Production Research Division, Development and Research Dept., Continental Oil Co., Ponca City, Okla.

T-1F Metallurgy
H. M. Cooley, Chairman; Bethlehem Steel Corp., 1908 First Nat'l. Bldg., Tulsa 2, Okla.
L. W. Vollmer, Vice Chairman; Gulf Research & Development Co., Drawer 2038, Pittsburgh, Pa.

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F. A. Prange, Chairman; Phillips Petroleum Co., Bartlesville, Okla.

T-1F-2 Sweet Crude and Sweet Condensate Stress Corrosion Cracking
J. P. Fraser, Chairman; Shell Development Co., 39 Claremont Drive, Orinda, Cal.

T-1H Oil String Casing Corrosion
W. C. Koger, Chairman; Cities Service Oil Co., Cities Service Building, Bartlesville, Okla.

TECHNICAL PRACTICES COMMITTEE
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T. J. Maitland, Vice Chairman; American Tel. & Tel. Co., 32 Avenue of the Americas, New York 13, N. Y.
L. L. Whiteneck, Vice President NACE; Plicoflex, Inc., 5501 Santa Fe Ave., Los Angeles 58, Cal.
Chairmen of T-1 through T-9 also are members of this committee.

T-1H-1 Oil String Casing Corrosion, West Texas, New Mexico Area
J. V. Gannon, Chairman; The Texas Co., Box 1270, Midland, Texas

T-1H-2 Oil String Casing Corrosion, West Kansas Area
A. S. Marken, Chairman; The Texas Co., Route #1, Great Bend, Kansas

T-1H-3 Oil String Casing Corrosion, East Texas Area
M. J. Olive, Chairman; Arkansas Fuel Oil Corp., General Engineering Department, Box 1117, Shreveport, La.

T-1H-4 Oil String Casing Corrosion, California Area
F. W. Schremp, Chairman; California Research Corp., Box 446, LaHabra, Cal.

T-1J Oil Field Structural Plastics
W. B. Sanford, Chairman; Mica Insulator Co., P. O. Box 1076, Schenectady 1, New York

T-1K Inhibitors for Oil and Gas Wells
A. H. Roebuck, Chairman; Production Research Div., Continental Oil Co., Ponca City, Okla.
E. J. Simmons, Vice Chairman; Sun Oil Co., Box 2880, Dallas, Texas

T-1K-1 Sour Crude Inhibitor Evaluation
J. A. Rowe, Chairman; Gulf Oil Corp., 5311 Kirby Drive, Houston, Texas
R. D. Stanphill, Vice-Chairman; Humble Oil & Refining Co., Box 2180, Houston, Texas

T-1K-2 Sweet Crude Inhibitor Evaluation
C. C. Nathan, Chairman; The Texas Co., Box 425, Bellaire, Texas
D. R. Fincher, Vice-Chairman; Tidewater Oil Co., 1538 Campbell Road, Houston 24, Texas

T-1M Corrosion of Oil and Gas Well Producing Equipment in Offshore Installations
R. M. Robinson, Chairman; Continental Oil Co., 206 Maritime Bldg., New Orleans 12, La.
O. L. Grosz, Vice Chairman; The California Co., Box 128, Harvey, La.

T-1M-1 Questionnaire and Screening
R. M. Robinson, Chairman; Continental Oil Co., 206 Maritime Bldg., New Orleans, La.

T-1M-2 Protective Barriers
H. E. Waldrip, Chairman; Gulf Oil Corp., 5311 Kirby Drive, Houston, Texas

T-1M-3 Cathodic
W. H. Edwards, Chairman; Superior Oil Co., 400 Oil & Gas Building, Houston, Texas

T-1M-4 Structural Design
D. B. Stauffer, Chairman; Humble Oil & Refining Co., Box 2180, Houston, Texas

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T 2   Pipe Line Corrosion

W. H. Stewart, Chairman; Sun Pipe Line Co., Box 2831, Beaumont, Texas
L. P. Sudrabin, Vice Chairman; Electro Rust-Proofing Corp., Box 178, Newark, N. J.

T-2A Galvanic Anodes
H. W. Wahlquist, Chairman; Ebasco Services Inc., 2 Rector St., New York, N. Y.

T-2A-2 Development of Standard Accelerated Galvanic Anode Test Procedures
H. A. Robinson, Chairman; The Dow Chemical Co., Midland, Mich.

T-2B Anodes for Impressed Currents
T. J. Maitland, Chairman; American Telephone & Telegraph Co., 32 Avenue of the Americas, New York 13, N. Y.
J. S. Dorsey, Vice Chairman; Southern California Gas Co., Box 3249, Terminal Annex, Los Angeles 54, Cal.
L. A. Hugo, Secretary; Engineering Department, Phillips Petroleum Co., Bartlesville, Okla.

T-2B-1 Sources of Impressed Current for Anodes
M. J. Olive, Chairman; Arkansas Fuel Oil Corp., Box 1117, Shreveport, La.

T-2B-2 Ground Bed Design Data
F. I. Dorr, Jr., Chairman; Dorr Engineering, Inc., 4626 Ingersoll, Houston, Texas

T-2B-4 Use of High Silicon Cast Iron for Anodes
W. L. Scull, Chairman; Colorado Interstate Gas Co., Box 1087, Colorado Springs, Colo.

T-2B-5 Use of Platinum, Palladium, etc. for Anodes
R. B. Teel, Chairman, The International Nickel Co., Inc., Box 262, Wrightsville Beach, N. C.

T-2C Minimum Current Requirements
R. M. Wainwright, Chairman; Good-All Electric Mfg. Co., Ogallala, Nebraska
Paul T. Miller, Vice Chairman; The Texas Pipe Line Co., Box 647, Almeda, Texas

T-2C-1 Basic Criteria
F. W. Ringer, Chairman, 7 Hampden Avenue, Narberth, Pennsylvania

T-2C-2 Coupons, As A Criteria For Cathodic Protection
H. J. Keeling, Chairman, Consulting Engineer, 1718 Livonia Avenue, Los Angeles 35, California

T-2C-3 History
Robert Pope, Chairman, Rd. 3, Box 302, Quakertown, Pennsylvania

T-2C-4 Cathodic Protection Criteria Research
L. P. Sudrabin, Chairman, Electro Rust-Proofing Corp., P. O. Box 178, Newark 1, New Jersey

T-2D Standardization of Procedures for Measuring Pipe Coating Leakage Conductance
Marshall E. Parker, Chairman; Cormit Engineering Co., 717A M & M Building, Houston, Texas
L. F. Heverly, Vice-Chairman; Trans-Canada Pipe Lines Ltd., 160 Bloor Street East, Toronto 5, Ontario, Canada

T-2D-1 Short Insulated Sections of Low Conductance
Marshall E. Parker, Jr., Chairman (See T-2D)

T-2D-2 Inaccessible Locations, Such as Water Crossings
H. V. Beezley, Chairman; United Gas Pipe Line Co., Box 1407, Shreveport, La.

T-2D-3 Parallel Lines
L. A. Hugo, Chairman; Phillips Petroleum Co., Bartlesville, Okla.

T-2D-5 Pipe Observed to Be in a Stray Current Field
H. W. Wahlquist, Chairman; Ebasco Services Inc., 2 Rector St., New York, N. Y.

T-2E Internal Corrosion of Product Pipe Lines and Tanks
Ivy M. Parker, Chairman; Plantation Pipe Line Co., Box 1743, Atlanta, Ga.
A. W. Jasek, Vice Chairman; Humble Pipe Line Co., Drawer 2220, Houston, Texas

T-2F Internal Corrosion of Crude Oil Pipe Lines and Tanks
E. R. Allen, Temporary Chairman; Humble Pipe Line Co., Drawer 2220, Houston, Texas

T-2G Coal Tar Coatings for Underground Use
T. F. P. Kelly, Chairman; Mavor-Kelly Co., 660 M & M Building, Houston 2, Texas
W. F. Fair, Jr., Vice Chairman; Koppers Co., Inc., Tar Products Div., Tech. Sec., 15 Plum St., Verona, Pa.

T-2H Asphalt Type Pipe Coatings
Austin S. Joy, Chairman; Brumley-Donaldson Co., 3050 East Slauson Avenue, Huntington Park, Cal.
P. E. Reynolds, Vice Chairman; Pacific Gas & Electric Co., 245 Market St., San Francisco, Cal.

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(See chairman T-2H)

T-2H-2 Criteria for Reporting on and Evaluating Underground Coatings
(See chairman T-2H)

T-2H-3 Specifications
(See chairman T-2H)

T-2H-4 Internal Pipe Treatment Specifications
F. B. Burns, Chairman; Kerr-McGee Oil Industries, Inc., Box 125, Wynnewood, Okla.

T-2J Wrappers for Underground Pipe Line Coating
Clark A. Bailey, Chairman; Johns-Manville Sales Corp., 22 East 40th St., New York 16, N. Y.
O. W. Wade, Vice Chairman; Transcontinental Gas Pipe Line Corp., Box 296, Houston, Texas

T-2J-1 Asbestos Felt
P. A. Meyer, Chairman; Nicolet Industries, Inc., 70 Pine St., New York, N. Y.

T-2J-2 Glass Wrap
E. J. Pennell, Chairman; Owens-Corning Fiberglas Corp., 902 American Airlines Bldg., Tulsa, Okla.

T-2J-3 Glass Base Outer Wrap
F. B. Burns, Chairman; Kerr-McGee Oil Industries, Inc., Box 125, Wynnewood, Okla.

T-2J-4 Rag Felt
L. S. Parker, Chairman; Pabco Industries, 475 Brannan St., San Francisco, Calif.

T-2J-5 Rock Shield
W. T. Ferrell, Chairman; Philip Carey Mfg. Co., Lockland, Cincinnati 15, Ohio

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T-2K Prefabricated Plastic Film for Pipe Line Coating
J. J. Wise, Chairman; Arkansas-Louisiana Gas Co., Box 1734, Shreveport, La.

H. D. Segool, Vice Chairman; The Kendall Co., Polyken Sales Division, 309 West Jackson Blvd., Chicago, Ill.

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H. D. Segool, Chairman

T-2K-2 Research and Development
H. A. Hendrickson, Chairman; Minnesota Mining & Mfg. Co., 900 Fauquier St., St. Paul, Minn.

T-2K-3 History and Results
F. E. Costanzo, Chairman; Manufacturers Light & Heat Co., 800 Union Trust Bldg., Pittsburgh, Pa.

T3 General

A. H. Roebuck, Chairman; Production Research Division, Continental Oil Co., Ponca City, Okla.

T-3A Corrosion Inhibitors
S.K. Coburn, Chairman; Association of American Railroads, 3140 South Federal St., Chicago, Ill.

L. C. Rowe, Vice Chairman; Research Staff, General Motors Corp., Box 188, North End Station, Detroit 2, Mich.

T-3A-1 General Theory of the Action of Corrosion Inhibitors
W. W. Sweet, Chairman; Research & Development Dept., Colgate Palmolive Co., 105 Hudson St., Jersey City, N. J.

T-3A-2 Methods of Testing & Screening Corrosion Inhibitors
(Chairman to be Selected)

T-3A-3 Materials Available for and Application of Corrosion Inhibitors
Lyle Timm, Chairman; Sharples Chemicals, Inc., Box 151, Wyandotte, Mich.

T-3B Corrosion Products
A. H. Roebuck, Chairman; Production Research Division, Continental Oil Company, Ponca City, Okla.

D. A. Vaughan, Vice Chairman, Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio.

T-3C Annual Losses Due to Corrosion
S. K. Coburn, Chairman, Association of American Railroads, 3140 South Federal Street, Chicago 16, Illinois

T-3D Instruments for Measuring Corrosion
E. H. Thalmann, Chairman; Ebasco Services, Inc., 2 Rector St., New York, N. Y.

F. W. Ringer, Vice Chairman; 7 Hampden Ave., Narberth, Pa.

T-3D-1 Electrical Holiday Inspection of Coatings
W.A. Broome, Chairman; Arkansas-Louisiana Gas Co., Box 1734, Shreveport, La.

T-3E Railroads
L. J. Nicholas, Chairman; The Pullman Co., Engineer of Research, Room 5-40, Merchandise Mart Plaza, Chicago, Ill.

G. M. Magee, Vice Chairman Assoc. American Railroads, 3140 South Federal Street, Chicago, Ill.

T-3E-1 Corrosion of Railroad Tank Cars
J. R. Spraul, Chairman; General American Transportation Corp., 150 West 151st Street, East Chicago, Ind.

C. M. Jekot, Vice Chairman; DeSoto Paint & Varnish Co., P. O. Box 186, Garland, Texas.

L. R. Honnaker, Vice Chairman, Engineering Materials Group, Eng. Dept., E. I. du Pont de Nemours & Co., Inc., 13W15 Louviers Bldg., Wilmington, Del.

T-3E-2 Corrosion in Railroad Hopper Cars
C. L. Crockett, Chairman; Norfolk and Western Railway, Motive Power Dept., Roanoke, Va.

T-3F Corrosion by High Purity Water
R. U. Blaser, Chairman; Research Center, Babcock & Wilcox Co., Box 835, Alliance, Ohio.

T-3F-1 Facilities for Production of High Purity Water

T-3F-2 Inhibitors
R. C. Ulmer, Chairman, Combustion Engineering Co., 200 Madison Avenue, New York, N. Y.

T-3F-3 Corrosion Products
R. U. Blaser, Chairman, Babcock & Wilcox Co., Alliance, Ohio.

T-3F-4 General Corrosion Problems
V. J. Payton, Chairman, Commonwealth Edison Co., 72 W. Adams St., Chicago, Ill.

T-3F-5 Declassification
J. L. English, Chairman, Oak Ridge National Lab., Box P, Oak Ridge, Tenn.

T-3F-6 Intercommittee Activities
E. P. Partridge, Chairman, Hall Labs., Box 1346, Pittsburgh, Pa.

T-3F-7 Bibliography
A. H. Roebuck, Chairman, Production Research Div., Continental Oil Co., Ponca City, Oklahoma.

T-3G Cathodic Protection
T. P. May, Chairman, The International Nickel Co., Inc., 67 Wall St., New York, N. Y.

T-3G-1 Cathodic Protection of Hull Bottoms of Ships
L. P. Sudrabin, Chairman, Electro Rust-Proofing Corp., Box 178, Newark, New Jersey.

T-3G-2 Cathodic Protection of Heat Exchangers
R. B. Teel, Chairman, The International Nickel Co., Inc., Box 262, Wrightsville Beach, N. C.

T-3G-3 Cathodic Protection of Process Equipment
A. A. Brouwer, Chairman, The Dow Chemical Co., Midland, Michigan.

T-3H Tanker Corrosion
W. S. Quimby, Chairman; Res. & Tech. Dept., The Texas Company, Box 509, Beacon, New York.

T4 Utilities

Irwin C. Dietze, Chairman, Dept. of Water & Power, Box 3669, Terminal Annex, Los Angeles, Calif.

T-4A Effects of Electrical Grounding on Corrosion
T. R. Stilley, Chairman; Good-All Electric Mfg. Co., Good-All Bldg., Ogallala, Neb.

T-4A-1 Recommendations for Materials to Be Used for Electrical Grounding to Reduce Corrosion
(Appointment of chairman pending)

T-4A-2 Recommendations for Grounding on Private Premises
Irwin C. Dietze, Chairman, Dept. of Water & Power, Box 3669, Terminal Annex, Los Angeles, Calif.

T-4B Corrosion of Cable Sheaths
T. J. Maitland, Chairman, American Telephone & Telegraph Co., 32 Avenue of the Americas, New York, N. Y.

H. M. Clayton, Vice Chairman; Memphis Gas, Light and Water Div., Box 388, Memphis, Tenn.

T-4B-1 Lead and Other Metallic Sheaths
T. J. Maitland, Chairman, American Telephone & Telegraph Co., 32 Avenue of the Americas, New York 13, New York.

T-4B-2 Cathodic Protection
J. J. Pokorny, Chairman, Cleveland Elec. Illuminating Co., 75 Public Sq., Cleveland 1, Ohio.

T-4B-3 Tests and Surveys
D. R. Werner, Chairman, American Telephone & Telegraph Co., 324 East 11th Street, Room 1701, Kansas City, Mo.

H. M. Clayton, Vice Chairman, Memphis Gas, Light and Water Div., Box 388, Memphis, Tenn.

T-4B-4 Protection of Pipe Type Cables
H. W. Dieck, Chairman, Long Island Lighting Company, 175 Old Country Road, Hicksville, New York.

J. B. Prime, Jr., Vice Chairman, Florida Power & Light Co., Box 3100, Miami, Florida.

T-4B-5 Non-Metallic Sheaths and Coatings
G. H. Hunt, Chairman, Simplex Wire & Cable Co., 79 Sidney St., Cambridge 39, Massachusetts.

C. L. Mercer, Vice Chairman, Southwestern Bell Tel. Co., Box 58, Westfield, Texas.

T-4B-6 Stray Current Electrolysis
J. Svetlik, Chairman, Northern Indiana Public Service Co., 5265 Hohman Ave., Hammond, Indiana.

G. H. Cantwell, Vice Chairman, Indiana Bell Telephone Co., 240 N. Meridian St., Indianapolis, Indiana.

T-4D Corrosion by Deicing Salts
D. W. Kaufmann, Chairman, International Salt Co., Inc., 638 Marine Trust Bldg., Buffalo, New York.

W. H. Bruckner, Vice Chairman, University of Illinois, Urbana, Illinois.

T-4D-1 Procedures for Conducting Field Tests Below Ground
F. E. Kulman, Chairman, Consolidated Edison Co. of New York, Inc., 4 Irving Place, New York, N. Y.

T-4D-2 Coordination of Field Programs Between Cities and Transportation Companies
George Illig, Chairman, Calgon, Inc., 323 Fourth Ave., Pittsburgh, Penn.

T-4E Corrosion by Domestic Waters
T. E. Larson, Chairman, Illinois State Water Survey, Box 232, Urbana, Illinois.

J. F. J. Thomas, Vice Chairman, Industrial Water Section; Dept. of Mines & Tech. Surveys; 40 Lydia Street, Ottawa, Ontario, Canada

T-4E-1 Hot Water Tank Corrosion
R. C. Weast, Chairman; Associate Professor of Chemistry, Case Institute of Technology, University Circle, Cleveland 6, Ohio.

T-4F Materials Selection for Corrosion Mitigation in the Utility Industry
F. E. Kulman, Temporary Chairman, Consolidated Edison Co. of New York, Inc., 4 Irving Place, New York, N. Y.

T-4F-1 Materials Selection in the Water Industry
Daniel Cushing, Chairman, 148 State St., Boston, Massachusetts.

Chester Anderson, Vice Chairman; Crane Company, 4100 South Kedzie Ave., Chicago 5, Ill.

Peter Kahn, Secretary; Metcalf & Eddy, 1300 Statler Bldg., Boston, Mass.

T-4F-2 Materials Selection in the Electric Industry

T5 Corrosion Problems in the Process Industries

R. I. Zimmerer, Chairman; Petro-Tex Chemical Corp., Box 2584, Houston, Texas.

C. P. Dillon, Vice-Chairman, Union Carbide Chemicals Co., Box 471, Texas City, Texas

T-5A Chemical Manufacturing Industry
C. P. Dillon, Chairman; Union Carbide Chemicals Co., Texas City, Texas

W. H. Burton, Vice-Chairman, General Chemical Division, Allied Chemical & Dye Corp., Camden 3, New Jersey

T-5A-1 Sulfuric Acid
W. A. Luce, Chairman, The Duriron Co., Box 1019, Dayton, Ohio.

T-5A-3 Acetic Acid
H. O. Teeple, Chairman, The International Nickel Co., Inc., 67 Wall St., New York, New York.

T-5A-4 Chlorine
L. W. Gleekman, Chairman; Wyandotte Chemicals Corp., 1609 Biddle Ave., Wyandotte, Mich.

T-5A-5 Nitric Acid
N. D. Groves, Chairman; Apartment 33-B, Brookline Manor, Reading, Pa.

F. H. Meyer, Vice Chairman; National Lead Co. of Ohio, Box 158, Mt. Healthy Station, Cincinnati 31, Ohio.

T-5A-6 HF Corrosion
T. L. Hoffman, Chairman, Phillips Petroleum Co., Atomic Energy Div., Box 1259, Idaho Falls, Idaho.

T-5B High Temperature Corrosion
E. N. Skinner, Chairman; The International Nickel Co., Inc., 67 Wall St., New York, N. Y.

J. L. McPherson, Vice-Chairman; 427 Murdock Ave., R.F.D. 2, Library, Pa.

T-5B-3 Oil Ash Corrosion
R. T. Foley, Chairman, General Electric Co., Schenectady, New York.

T-5B-5 Corrosion by Molten Salts and Metals
W. D. Manly, Chairman; Union Carbide Nuclear Co., Oak Ridge National Lab., Box P, Oak Ridge, Tenn.

T-5C Corrosion by Cooling Waters

T-5C-1 Corrosion by Cooling Waters (South Central Region)
C. P. Dillon, Chairman; Union Carbide Chemicals Co., Texas City, Texas.

M. Brooke, Vice Chairman; Phillips Petroleum Co., Sweeny Refinery, Sweeny, Texas.

W. W. Wheeler, Secretary; Rohm & Haas, Box 672, Pasadena, Texas.

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T-5D Plastic Materials of Construction
S. W. McIlrath, Chairman, 151 East 214th St., Euclid, Ohio.

R. E. Gackenbach, Vice-Chairman; American Cyanamid Co., Organic Chemical Div., Bound Brook, N. J.

T-5D-1 Questionnaires
S. W. McIlrath, Chairman, 151 E. 214th Street, Euclid 23, Ohio.

T-5D-2 Inorganic Acids
R. L. Hughes, Chairman, Spencer Chemical Co., 1231 Woodswether Rd., Kansas City, Missouri.

J. F. Malone, Secretary, B. F. Goodrich Chemical Co., 2060 East Ninth Street, Cleveland 15, Ohio.

T-5D-3 Inorganic Alkalies
Peter Kimen, Chairman, Champion Paper & Fibre Co., Box 872, Pasadena, Texas.

L. B. Connelly, Secretary, Eastman Chemical Products Company, 704 Texas National Bank Building, Houston 2, Texas.

T-5D-4 Gases
Beaumont Thomas, Chairman, Stebbins Eng. & Mfg. Co., Eastern Blvd., Watertown, New York.

J. L. Forse, Vice Chairman, Dow Chemical Company, Plastics Technical Service, Midland, Michigan.

William Eakins, Secretary; Chemical Corp., Pla-Tank Division, West Warren, Mass.

T-5D-5 Water and Salt Solutions
Paul Elliott, Chairman, Naugatuck Chemical Company, Kralastic Development, Naugatuck, Conn.

T-5D-6 Organic Chemicals
B. B. Pusey, Chairman; Bakelite Company, Division Union Carbide Chemicals Co., Bound Brook, N. J.

Wade Wolfe, Jr., Secretary, 73 Ermann Drive, Buffalo 17, New York.

T-5D-7 Engineering Design
O. H. Fenner, Chairman, Monsanto Chemical Company, 1700 South Second Street, St. Louis 4, Missouri.

K. A. Phillips, Vice-Chairman, American Zinc, Lead & Smelting Co., P. O. Box 495, East St. Louis, Illinois.

W. B. Meyer, Secretary, St. Louis Metallizing Co., 625 South Sarah, St. Louis 10, Missouri.

T-5D-8 Methods and Criteria for Evaluating Plastics in Chemical Environment
R. F. Clarkson, Chairman, Olin Mathieson Chemical Corp., Mathieson Building, Baltimore, Md.

R. Lembcke, Secretary, Cities Service Res. & Dev. Co., 920 East Third, Tulsa 3, Oklahoma.

T-5E Stress Corrosion Cracking of Austenitic Stainless Steel
L. Miller Rogers, Chairman; Union Carbide Chemicals Co., Box 471, Texas City, Texas.

E. V. Kunkel, Vice Chairman; Celanese Corp., Box 148, Bishop, Texas.

T6 Protective Coatings

L. S. Van Delinder, Chairman; Union Carbide Chemicals Co., Development Dept., South Charleston, W. Va.

O. H. Fenner, Vice-Chairman; Monsanto Chemical Co., 1700 South Second St., St. Louis 4, Mo.

T-6A Organic Coatings and Linings for Resistance to Chemical Corrosion
C. G. Munger, Chairman; Amercoat Corp., 4809 Firestone Blvd., South Gate, Cal.
L. S. Van Delinder, Vice Chairman; Union Carbide Chemicals Co., Development Dept., South Charleston, W. Va.
J. I. Richardson, Secretary; Amercoat Corp., 4809 Firestone Blvd., South Gate, Cal.

T-6A-1 Heavy Linings
H. C. Klein, Chairman; B. F. Goodrich Co., 500 South Main St., Department 0716-Bldg. 25C, Akron, Ohio.

T-6A-2 Vinyl Coatings
K. Tator, Chairman, 2020 Montour Street, Coraopolis, Pa.

T-6A-3 Vinylidene Chloride Polymers
R. L. Brown, Chairman, The Dow Chemical Co., Midland, Mich.

T-6A-4 Phenolics
Forest Baskett, Chairman; Sheet Metal Engineers, Inc., Box 9094, Houston 11, Texas.

T-6A-5 Polyethylene
L. S. Van Delinder, Chairman, Carbide & Carbon Chemicals Co., South Charleston, W. Va.

T-6A-6 Rubber and Elastomers
H. C. Klein, Chairman; B. F. Goodrich Co., 500 South Main St.; Department 0716-Building 25C, Akron, Ohio.

T-6A-7 Silicones
R. McFarland, Jr., Chairman, Hills-McCanna Co., 3025 N. Western Ave., Chicago, Ill.

T-6A-8 Methyacrylates

T-6A-9 Furanes

T-6A-10 Polyesters
D. D. Cone, Chairman; Texas Butadiene & Chemical Corp., Box 777, Channelview, Texas.

T-6A-11 Epoxys
C. G. Munger, Chairman, Amercoat Corp., 4809 Firestone Blvd., South Gate, Cal.

T-6A-12 Fluorocarbons
L. A. Ferris, Chairman, E. I. Du Pont de Nemours & Co., Inc., Wilmington, Delaware.

T-6A-13 Chlorinated Rubbers
Appointment Pending

T-6A-14 Organic-Brick Covered
R. W. Hall, Chairman, Stebbins Engr. & Mfg. Co., 363 Eastern Blvd., Watertown, N. Y.

T-6A-15 Rigid Vinyls
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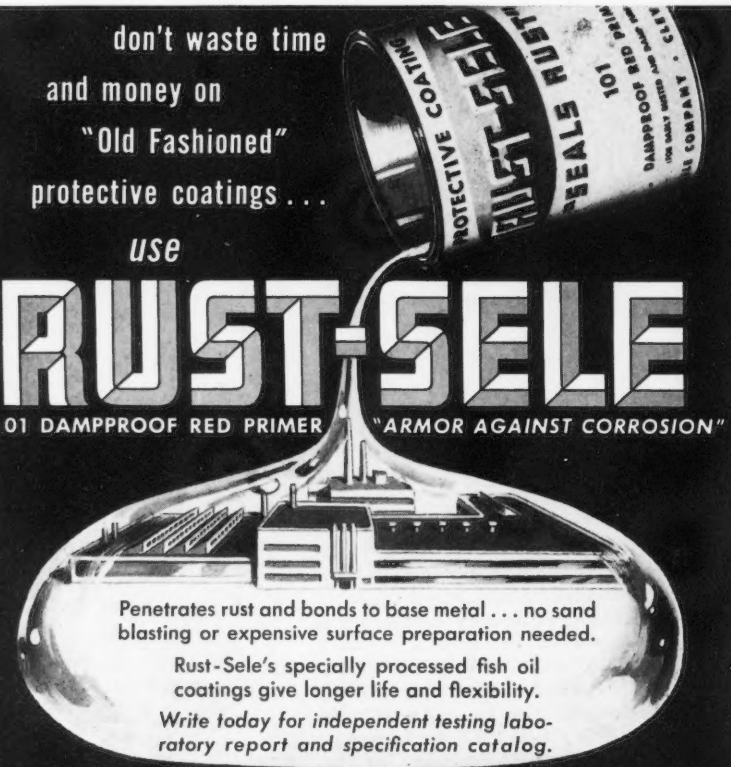
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(a) To promote the prevention of corrosion, thereby curtailing economic waste and conserving natural resources.

(b) To provide forums and media through which experiences with corrosion and its prevention may be reported, discussed and published for the common good.

(c) To encourage special study and research to determine the fundamental causes of corrosion, and to develop new or improved techniques for its prevention.

(d) To correlate study and research on corrosion problems among technical associations to reduce duplication and increase efficiency.

(e) To promote standardization of terminology, techniques, equipment and design in corrosion control.

(f) To contribute to industrial and public safety by promoting the prevention of corrosion as a cause of accidents.

(g) To foster cooperation between individual operators of metallic plant and structures in the joint solution of common corrosion problems.

(h) To invite a wide diversity of memberships, thereby insuring reciprocal benefits between industries and governmental groups as well as between individuals and corporations.

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Corrosion

Corrosion Research in Progress

Effect of Dissolved Oxygen on Corrosion And on Cathodic Protection Requirements

By G. A. MARSH* and E. SCHASCHL*

Introduction

PURE OIL Company's Research and Development Laboratories are engaged in a variety of corrosion projects, one of the more general ones being a study of the effect of dissolved oxygen on corrosion and on cathodic protection. The interrelationship of corrosion rate of steel, dissolved oxygen concentration, agitation, electrode potential, and cathodic protection current density are being studied under controlled laboratory conditions. Another related subject being studied is differential aeration. The effect of variable oxygen concentrations, spatial relationships, and relative areas of anode and cathode are being determined.

Test Procedure

The basic tool used in these studies is the temperature-compensated corrosion test probe, which was reported by these Laboratories in 1955.[1] With this probe, it is possible to make continuous, direct observations of corrosion loss while the specimen or probe is immersed in a corrosive environment, without having to remove the specimen. While this method has disadvantages inherent in using small test pieces, it greatly facilitates laboratory testing and certain field testing.

The dissolved oxygen measurements are being made by means of a calibrated rotating platinum electrode.[2] This method is free from some of the objections of the conventional test; it requires only a small sample, and yields results in a few seconds rather than minutes.

Preliminary Results

Preliminary results of the work now in progress have indicated that, while the corrosion rate of steel is essentially a linear function of dissolved oxygen in neutral solutions, the rate falls almost to zero near 1.0 ppm dissolved oxygen rather than at zero ppm dissolved oxygen as commonly assumed. In the region below 2 ppm dissolved oxygen, there is almost no effect of agitation on corrosion rate; above 2 ppm there is a large effect. In neutral environments, where corrosion is under cathodic control, the minimum current density needed for protection is about 20 percent greater than the current associated with corrosion. By measuring the corrosion rate of an unprotected specimen, it should be possible to compute the minimum current density needed for cathodic protection in the field.

In acidic environments, less current is needed for protection than is predicted by analysis of the mechanism of cathodic protection. This fact suggests that the anodic reaction in low pH corrosion proceeds by the removal of "chunks" of metal which contain several atoms. The "chunk effect" also appears to operate in the neutral range, but only when the corrosion rate is very high.

Differential Aeration

Differential aeration so far appears to be an important factor in corrosion if a structure is buried at the water table. In a static liquid-saturated porous system, however, there is no appreciable effect of differential aeration even when the bulk oxygen concentrations at the anodic and cathodic areas are widely different. Some of the data obtained so far have been described in a paper presented at the 1956 South-Central Regional Meeting of The Natural Association of Corrosion Engineers.[3]

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* The Pure Oil Company, Research and Development Laboratories, Crystal Lake, Illinois.

Factors Other Than Mineral Content Which Influence the Corrosiveness of Cooling Water*

By E. H. HURST

E. H. HURST received a BS in chemistry from Michigan State University in 1949. Joining the National Aluminate Corporation, Chicago, Illinois in 1953, he has specialized in the development and application of stabilization and microbiological control chemicals in cooling tower systems. He currently serves as Product Manager, Water Stabilization Chemicals.

Introduction

IN MANY WAYS the treatment of cooling water systems parallels the development of boiler and boiler feedwater treatment. Not too many years ago the boiler operator was concerned primarily with scale, paying relatively little attention to other problems such as corrosion, carryover, and fireside deposits. Similarly, the problems in cooling tower systems years ago involved primarily the question of scale.

The problems faced in cooling tower systems are as complex as those in boiler feedwater treatment and in many instances more so. However, many of the factors which contribute to the complexity of treatment of cooling tower systems until recently had not been given the attention which they deserve.

In evaluating the corrosiveness of a cooling tower water, consideration sometimes is limited to the mineral nature of the water to be used. This is an extremely important consideration, since the water may be either scale-forming, or corrosive in nature, or both. Langelier[1] and Ryznar[2] have provided useful tools in their Saturation and Stability Indices for determining the nature of the water. Consideration also should be given to the dissolved gases present in the water and the nature of the dissolved solids.

Although the mineral characteristics of the water to be used in the cooling system are extremely important, they are by no means the only items to be considered. Other factors that should be considered are the presence of dissimilar metals in the system, sludge deposits from either a chemical reaction or a microbiological reaction, turbidity and suspended matter, and hydrocarbon pollution. Also of vital interest in the over-all program is the protection of the cooling water itself from chemical or microbiological attack.

Dissimilar Metals

The presence of dissimilar metals in a cooling system is very common; however, the use of two or more different metals in a system can produce serious corrosion problems. The rate of corrosion in the galvanic cell is influenced by the conductivity of the corroding medium (in this case the system water). High concentrations of dissolved solids (electrolyte) can result in highly active galvanic cells.

Metals which normally would be cathodic can also corrode, particularly when deposits form on the metal surface, setting up localized differential con-

Abstract

There are several factors other than mineral constituents which determine the corrosiveness of a cooling water. These factors include microbiological activity, silt and debris, suspended solids, dissimilar metals and hydrocarbon pollution. The complete effective performance of a cooling water corrosion prevention program cannot be realized without controlling these factors.

Data are given to show the effect of summer and winter slime on corrosion rates in the presence of an inhibitor.   4.6.4

centration cells. The corrosion products from these cells could cause serious corrosion should they lodge elsewhere and plate out as the free metal, setting up galvanic corrosion cells.

Design of heat exchange equipment with more and more extensive use of copper and copper alloys also should include provision for prevention of galvanic corrosion. Methods which may be considered for elimination of the galvanic couples include the use of coatings, such as plastic or rubber, or the application of cathodic protection.

Removal of the galvanic corrosion potentials, either through design or other suitable methods, means one less factor to contribute to the corrosiveness of the system water.

Turbidity and Suspended Matter

Turbidity or suspended matter, in addition to appearing naturally in the water supply, may also be the result of improper or incomplete pretreatment of the water in either a clarification or softening step. The suspended matter settles out in areas of low velocity, or can be washed against the surface of the channel head or tube sheet with such force that it adheres. With the deposition of the suspended matter on the metal surface, localized pitting type of

attack and tuberculation may occur, caused by the differential aeration-type of corrosion cell.

Although mention was made of the presence of turbidity and suspended matter in the system as a result of either a poor quality makeup water or improper treatment of the makeup water, an even more important source of suspended matter is inherent in the nature of operation of cooling towers. These systems are exposed to the air and to many weather and atmospheric conditions. They operate as mammoth air washers, scrubbing the air which passes through to cool the water and collecting the airborne dirt and other foreign materials. This is a principal source of suspended matter in many areas and contributes to the suspended matter of the water and to the corrosive potential, through formation of corrosion cells where these materials settle out.

Chemical treatment of a cooling system water to protect the metals is handicapped greatly in the presence of the suspended matter and foreign materials. The chemical corrosion inhibitors rely upon their ability to continually repair the protective film. The deposition or settling out of material shields the surfaces of the metal from contact with the chemically treated water and the corrosion process starts.

Generally, a flow velocity of three feet per second will minimize deposition of suspended matter and thus reduce another contributing factor to the corrosive potential of a cooling water. Another useful tool for controlling suspended matter is the installation of a side stream filter.

Process Pollution

Process pollution of cooling system water occurs quite frequently and should be considered in evaluating the corrosive potential in a system. One of the most common pollutants is hydrocarbon with accompanying sulfides and mercaptans. These pollutants normally are considered to be corrosive; however, of more importance is perhaps their ability to consume chlorine used for microbiological control. In the absence of adequate control measures, the microbiological organisms thrive and probably account for a greater portion of the resultant corrosion than is realized.

Other process pollutants serve as nutrients for the bacteria in the system. Ammonia can serve as a nutrient for certain types of bacteria. Other nutrients are sugars, food products, and various organics.

Microbiological Contamination

Microbiological contamination in a cooling system may result either from accumulation of airborne organisms or from the use of highly contaminated makeup water. Continuous treatment of the makeup water may produce an essentially sterile water; however, the airborne organisms can thrive quite readily in the system. Cooling towers located near breweries or food processing plants are particularly vulnerable to inoculation of the system with airborne organisms. Those towers which are exposed to wind-swept fields from which dirt is blown are vulnerable particularly to sulfate-reducing bacteria which thrive in the dirt or soil. Other foreign material blown into the system such as leaves, paper or wood, decomposes to form nutrients for the growth of bacteria.

The presence of heavy microbiological activity in a cooling system can be detrimental for several reasons. The organisms capable of forming slime cause plugging of tubes and low water flow through units. The slime deposits are very good insulators and result in poor heat exchange coefficients.

Of extreme importance is the role of the microbiological organisms in corrosion. Deposits of microbiological organisms produce differential aeration or concentration cells. Certain organisms may utilize mineral components and produce corrosive wastes.

The types of micro-organisms found in a cooling system are of significance in evaluating corrosion potentials. The identity of the organisms as to specific scientific nomenclature is not as important as the classification of the organisms into groups based on their nature or behavior in the system. Whether the organisms are *Flavobacterium* or *Aerobacter* is of minor importance as compared to the fact that both of these organisms are slime-producing organisms.

Microbiological organisms found in cooling systems can be classified as fungi, algae, and bacteria. The fungi which are common in cooling systems are the molds and yeasts. These are extremely large organisms as compared to bacteria and are more resistant to killing dosages of chemical. The algae encountered in cooling tower waters can be classified as the green or blue-green algae, which are similar in nature, and the diatoms which result in silica deposits. The bacteria can be divided into functional classifications: slime-forming, sulfate-reducing, iron-depositing and non-troublesome groups.

Rarely, if ever, are deposits or growths of one particular types or species found. The conditions of the system are such as to provide suitable environment for all types. Each type of organism prefers its own peculiar environment, an environment which may be produced by other types of organisms. The living together of different types of organisms to their mutual benefit is known as symbiosis.

Probably the most significant corrosion-producing organisms found in cooling systems are the sulfate-reducing bacteria. There are several organisms grouped under this classification, all of which are characterized by their ability to utilize sulfur compounds, such as the sulfates, in their metabolic processes to produce sulfides.

Although the sulfate-reducing bacteria are considered to be anaerobic in nature,[3] they are quite common in highly aerated systems such as cooling towers. The presence of other organisms in the system in the form of deposits shields the sulfate reducers and produces the anaerobic conditions necessary for their rapid growth. Also debris or dirt in the system may serve this purpose.

The action of the sulfate-reducing bacteria in the corrosion process is considered to be one of a depolarizer. The organisms utilize sulfates which are reduced to sulfides, and as with all chemical equations, reduction must be accompanied by oxidation.
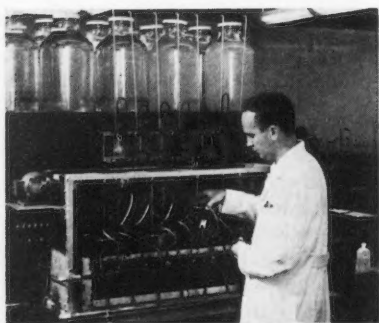
Figure 1—Laboratory equipment for bacterial corrosion studies.
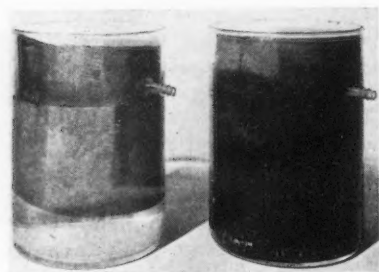
Figure 2—Laboratory test vessels with stainless steel screens showing conditions before and after slime growth.
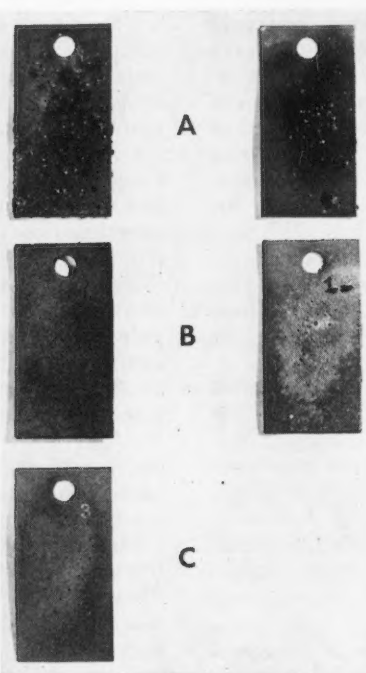
Figure 3—Test coupons after test with summer slime conditions; synergized polyphosphate type inhibitor was used. Code to letters is as follows: A—mixed slime plus sulfate reducers; B—mixed slime; C—no slime present.
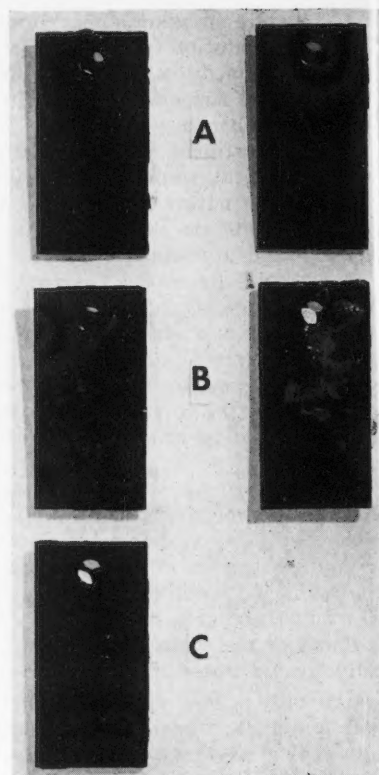
Figure 4—Test coupons after test with winter slime conditions; chromate-polyphosphate type inhibitor was used. Code to letters is as follows: A—mixed slime plus sulfate reducers; B—mixed slime; C—no slime present.

Organic acids, hydrocarbons, carbohydrates and hydrogen are readily oxidizable materials found in the system.[3] The hydrogen is present as a polarizing film on the metal surface and as long as this film remains intact, the corrosion process is stifled. The film may be removed by depolarizer agents such as oxygen, forming water. The sulfate reducers act as depolarizers, but by a slightly different mechanism.[4]

Anodic　　　　　　　　$-4Fe \rightarrow 4Fe^{++} + 8e$
Cathodic　　　　　　　$-8H_2O + 8e \rightarrow 8H + 8OH^-$

Bacteria depolarization　$-8H + CaSO_4$ bacteria $4H_2O + CaS$
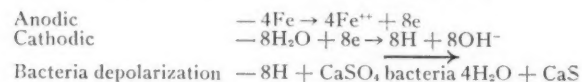
The result is intensified, localized corrosion or pitting which is more objectionable than general corrosion involving the same magnitude of metal loss because it is more conducive to the development of leaks.

TABLE 1—Mineral Composition of Test Water

Dissolved Solids	2,000 ppm
Total Hardness (as $CaCO_3$)	400 ppm
Calcium Hardness (as $CaCO_3$)	250 ppm
Magnesium Hardness (as $CaCO_3$)	150 ppm
Total Alkalinity	*
pH	*
Chlorides (as NaCl)	500 ppm
Sulfates (as Na_2SO_4)	1,400 ppm
Silica	2 ppm
Iron	0.2 ppm

* Alkalinity approximately 100 ppm and pH 7.0 to 7.5 for chromate-polyphosphate treatment, alkalinity approximately 8 ppm and pH 6.0 to 6.5 for synergized polyphosphate type treatment.

Other Corrosive Bacteria

There are other types of bacteria which are corrosive, but which are not encountered frequently. These include sulfur bacteria which have been described in literature as capable of producing sulfuric acid from sulfur sources.[5] Also, bacteria capable of producing nitric acid from ammonia have been reported,[6,7] and since the original report, have been detected several times.

Slime-Forming Bacteria

The presence of slime-forming bacteria results in large adherent masses which plug equipment and restrict flow. They reduce heat transfer rates and are instrumental in corrosion by setting up differential aeration or concentration cells with corrosion taking place beneath the deposit. They also serve to shield the anaerobic sulfate-reducing bacteria.

TABLE 2—Types of Bacteria Used for Inoculation

Slime-forming bacteria:
　Aerobacter aerogenes
　E. coli
　Pseudomonas sp
Other types not known to be primarily slime-formers.

Note:　In addition to the above bacteria, sulfate-reducing bacteria, *Desulfovibrio desulfuricans*, were added to the "A" baths.

Laboratory Research

Although investigators are agreed that microorganisms can cause corrosion, very little has been published on the amount of corrosion to be experienced from this source. In an effort to correlate the corrosion rates experienced in a system free of microbiological contamination and those of a highly polluted system, National Aluminate's laboratories undertook a study of the problem. The project was undertaken despite the realization that results might not be reproducible and that difficulty might be experienced in getting the slime to adhere to the clean, prepared surface of the laboratory metal specimens.

The project was carried out in laboratory equipment designed to simulate cooling tower system water conditions. This equipment consisted of five water baths held at a constant temperature of 120 F in an oil bath. Mineral content of the water is given in Table 1. The water was agitated with paddles continuously and aerated through porous diffusers. The laboratory specimens used were mild steel coupons, sand blasted and suspended in the bath on glass hooks. The baths were constantly overflowed to duplicate the blowdown and windage loss obtained in a cooling tower system. To help in growing the microbiological organisms, stainless steel screens were inserted vertically inside the circumference of the bath and Berl Saddles or acid cleaned gravel placed in the bottom of each bath. The laboratory equipment is shown in Figures 1 and 2. Each of the four test baths was inoculated with slime taken from actual cooling tower systems. Types of bacteria used for inoculation can be found in Table 2. After the growths had been established over several days' period, the coupons were inserted and the test begun.

The tests were run in duplicate to check the reproducibility of the results. Thus, two baths were inoculated with mixed slime and sulfate-reducing bacteria and two baths with mixed slime only (no sulfate-reducing bacteria). A fifth bath was used as a blank with only the corrosion inhibitor present in the other baths added to it.

Two series of tests were run to determine the effect of two common, widely used, inhibitors against microbiological corrosion. The inhibitors used were the synergized polyphosphate and a combination of sodium chromate and polyphosphate. One series was carried out in the summer (summer slime) and the other series in the winter (winter slime) to take into consideration the different growth characteristics of the organisms according to season. Data from these tests can be found in Tables 3 and 4. The comparison between winter and summer slime growths was made using the synergized polyphosphate inhibitor.

Note in Figure 3 the appearance of the specimen used for summer slime using the synergized polyphosphate and in Figure 4 the winter slime using the chromate-polyphosphate treatment. Some difficulty was experienced in getting the slime to adhere to the panels in the synergized polyphosphate treated system even in the summer tests, and no slime was recorded by picture in the winter tests. However, with the chromate-polyphosphate, better adherence was obtained.

The comparison of corrosion rates between winter and summer slime conditions with the synergized polyphosphate at the end of eleven days' exposure was:

> Summer slime — 4.0 mpy
> Winter slime — 2.4 mpy
> No slime   — 1.9 mpy

In this connection refer to Figure 5.

The corrosion rates with winter slime on chromate-polyphosphate inhibited systems are shown in Figure 6. The initial high rate probably is the result of the ease of adherence to these specimens. The final rates are approximately double the no slime rate.

In the tests containing sulfate-reducing bacteria, severe localized attack was noted. Only minor localized attack was detected in the tests using the mixed slime. Tests on summer slime and chromate-polyphosphate, on the basis of this data, could be expected to show even higher corrosion rates. However, since the test was not performed and in view of the activity of the growth of the organism, no definite conclusion should be drawn.

No test data were obtained on copper or other non-ferrous metals. Although corrosion of Admiralty tubes by bacteria has been reported[8] it would be advisable to determine the degree of attack.

TABLE 3—Summer Slime Effect on Corrosion[1]

	3 Days	7 Days	11 Days	15 Days
A—Mixed slime plus sulfate reducers	3.5 3.6	4.7 3.4	4.3 3.7	4.3 4.0
B—Mixed slime	5.1 2.6	2.9 2.1	2.3 4.2	2.1 2.8
C—No slime	2.6	2.0	1.9	2.0

[1] Corrosion rates in mils per year.

Conditions of Test

Temperature	120 F.
Inhibitor (Synergized polyphosphate type)	35 ppm total PO₄
pH	6.0–6.5
Water composition	See Table 1
Source of slime	Cooling tower systems
Aeration	Continuous
Agitation	Paddle
Coupons	Mild steel, sand blasted, 1″ x 2″

TABLE 4—Winter Slime Effect on Corrosion[1]

	Corrosion Inhibitor	3 Days	7 Days	11 Days
A—Mixed slime plus sulfate reducers	Chromate-polyphosphate	5.6 9.1	3.5 5.6	2.6 5.2
	Synergized polyphosphate	4.8 4.4	2.8 2.7	2.5 2.3
B—Mixed slime	Chromate-polyphosphate	8.1 16.2	4.5 5.8	3.1 4.3
C—No slime	Chromate-polyphosphate	4.6	3.0	2.0

[1] Corrosion rates in mils per year.

Conditions of Test

Temperature	120 F.
pH (Synergized polyphosphate)	6.0–6.5
pH (Chromate-polyphosphate)	7.0–7.5
Water composition	See Table 1
Source of slime	Cooling tower systems
Aeration	Continuous
Agitation	Paddle
Coupons	Mild steel, sand blasted. 1″ x 2″
Inhibitor (Chromate-polyphosphate)	50 ppm CrO₄—5 ppm total PO₄
Inhibitor (Synergized polyphosphate)	35 ppm total PO₄
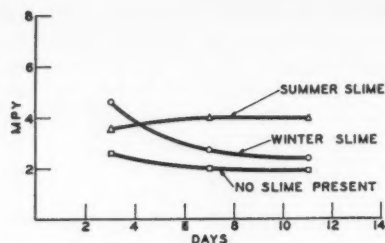
Figure 5—Corrosion rates of synergized polyphosphate type treatment with mixed slime plus sulfate reducers.

Figure 6—Corrosion rates of chromate-phosphate treatment with winter slime conditions.

The amount of corrosion taking place is a function of the adherence of the slime. In the laboratory and in the field there is no means of determining the amount of surface area which will be covered by slime. It is common to have one piece of equipment heavily covered with slime, and have another piece in the same system not so covered. However, the conclusion can be drawn that as long as the organisms are not adherent, the corrosion rates on steel are not adversely affected.

The test data obtained show a definite adverse effect on corrosion rates of steel by the presence of microbiological growth. The increase may vary from 25 to 100 percent according to the data. In the presence of an inadequate corrosion inhibitor, even greater increases would be expected. The seriousness of corrosion from microbiological organisms certainly justifies good control of the organisms in the cooling system from the standpoint of corrosion alone, even if there were not other adverse consequences of microbiological growth, such as reduced heat transfer, restriction of water flow, etc.

Conclusion

An effort has been made to show the many factors which must be considered in protecting a system from corrosion. In addition to mineral content of the system water, slime and microbiological activity, different metals, dirt and debris, turbidity and suspended matter, also influence the corrosion rate. Good corrosion control can be obtained only if these other factors are considered and taken into account. Failure to control these factors may result in failure of any effective chemical corrosion prevention treatment. Control of many of the factors may be grouped under one term, good housekeeping. Maintaining the system free from slime, debris, dirt, turbidity, is a function of cleanliness. Good housekeeping and cleanliness are synonymous with high standards. If high standards of performance of cooling water corrosion prevention programs are desired, then certainly good housekeeping is essential.
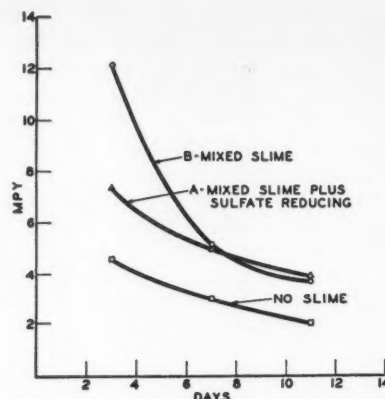
At the present time the author has no data available on the effect of suspended matter and debris on the corrosion rates in a cooling tower system. Such data, while highly desirable, would be difficult to obtain in the laboratory. It is hoped that the data presented here on the influence of micro-organisms will serve to develop more interest and activity in considering these other factors which influence the corrosiveness of a cooling tower water.

Acknowledgment

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Any discussions of this article not published above will appear in the December, 1957 issue.

Non-Chemical Factors Affecting Inhibitor Selection And Performance in Air Conditioning Cooling Waters*

By SIDNEY SUSSMAN

Introduction

THE RAPID increase in the use of air conditioning has multiplied cooling-water corrosion problems. The high seasonal peaks in water consumption resulting from air conditioning cooling demands have caused virtually all of the larger municipalities to adopt ordinances requiring the installation of. water conservation equipment.

Although a cooling tower or evaporative condenser is designed to provide optimum evaporation of water, it is also a good air scrubber. In a large proportion of installations in urban locations, the air scrubbed by such equipment contains a rather high proportion of solid and gaseous pollutants[1] which can aggravate corrosive conditions already present as a result of the air saturation of the circulating water in evaporative cooling and humidifying equipment.[2] Table 1 shows several typical examples of the corrosive conditions which develop in untreated circulating cooling waters in large cities.

Fundamentally. the chemical problems of corrosion control do not differ from those of other types of water-handling equipment. However, in typical urban air-conditioning systems, non-chemical factors play a disproportionately large part in corrosion control.

Many non-chemical difficulties in handling corrosion problems in these systems are due to their relatively small size. The greatest number of urban air conditioning systems have from 10 to 500 tons of refrigeration capacity. In recirculating systems, these circulate from 30 to 1,500 gallons of cooling water per minute. Although corrosion control principles apply equally to these systems, the great variety of other influences prevents the application of pat formulas, and requires a thorough exploration of existing conditions at each location if successful results are to be obtained.

Typical non-chemical problems encountered in handling corrosion control in urban air conditioning systems are discussed under four major headings: Economic, mechanical, human and legal factors. Case histories illustrate many of the points discussed.

Economic Factors

Equipment Cost

Because the typical urban air-conditioning system is installed in a store or office of modest size, there is a tendency to economize in making the original installation, without considering the effect upon satisfactory performance or life of the equipment.

SIDNEY SUSSMAN is chief chemist for Water Service Laboratories, New York City. He has a BS from Polytechnic Institute of Brooklyn and a PhD from Massachusetts Institute of Technology in 1937. Before joining his present employer in 1949 he was employed by the DuPont Company, the Permutit Company and Liquid Conditioning Corp. His principal work is in corrosion control in water systems. He has authored more than 20 papers and patents. He is a member of NACE, ACS, AWWA and other technical groups and was first president of Metropolitan Water and Wastes Society.

Abstract

The rapid growth of air conditioning, particularly in urban areas, has multiplied cooling water corrosion problems. The effectiveness of corrosion control by chemical inhibitors in these systems is subject to non-chemical factors to a degree not usually encountered in the larger industrial cooling systems. These considerations include economic, mechanical, human and legal factors. The use of untrained personnel for equipment operation and maintenance can restrict the choice of inhibitor or negate an otherwise satisfactory corrosion control program, as well as increase safety hazards.

Selection of the inhibitor and its use are restricted in many cases by legal requirements pertaining to cross-connections, water conservation, or waste disposal. Equipment location, rarely considered from the viewpoint of maintenance and corrosion control, is frequently a factor in the choice of inhibitor and in its effectiveness.

Attempts to keep equipment and operating costs low frequently have secondary effects upon corrosion control. **4.6.4**

The constant pressure to keep down the cost of equipment results in an installation whose capacity is frequently borderline or in some cases undersized for the cooling needs of the location. When midsummer hot spells arrive, the temperature can be reduced to the desired level only by furnishing additional cooling. Frequently this is done by running city water into the pan of the cooling tower or evaporative condenser which, of course, causes an overflow. In addition to wasting water, it carries excessive amounts of water-treatment chemicals to the sewer, often making it almost impossible to maintain necessary concentrations of corrosion inhibitors.

Much of the equipment is sold on the basis that while initial expense may be high, operating expense will be limited to the cost of make-up water and electric power. Under such circumstances the necessity for water treatment is rarely pointed out to the

dope, metal chips, and other construction debris. Good practice calls for a chemical cleaning of the water circuit in order to avoid mechanical clogging or localized corrosion effects which can result if this dirt is left in when operations start. Unfortunately, such a cleaning is often omitted as an economy measure.

When a desire for economy results in rejection of an adequate corrosion-control program, there is a tendency to rely upon the use of purchased "compounds." These "compounds" generally are added to the pan of the equipment once or twice a day. Such slug feeding results in a periodic peak in the inhibitor concentration followed by a steady reduction so that either excessive quantities of chemicals are used or there is too little inhibitor during a part of each day. Figure 1 illustrates these effects of slug feeding showing how a single daily dose may use three to four times the amount of inhibitor needed for good treatment with continuous feeding.

In a limited number of cases, well waters used for cooling on a once-through basis are extremely corrosive. Figure 2 shows a section of steel pipe which failed after 18 months in a once-through cooling system carrying a low solids, high carbon dioxide well water. These cases generally arise from failure to take the elementary precaution of analyzing the well water before specifying materials of construction. Because the large volume of water to be treated makes inhibitor addition expensive, it often is neglected until the equipment fails.

"Gadgets"

In an attempt to avoid the cost of legitimate corrosion control treatment the economy-minded owner frequently falls into the hands of glib salesmen of various pseudo-scientific water-treating gadgets. In every case that the author has seen, the results of relying upon such equipment in a corrosive environment have been disastrous. Even if conditions are not sufficiently severe to cause rapid failure, operation with these gadgets permits the accumulation of corrosion products which make much more difficult the protection of the system by effective inhibitors at a subsequent time.

Table 3 summarizes test coupon results obtained in a New York City cooling tower equipped with a fitting in which a permanent magnet was mounted as compared with results obtained in untreated and chromate-treated units in the area. Table 4 shows typical analyses of makeup and circulating water in the gadget-equipped cooling tower during the test period. The sales literature for this device, offering it as a cure for almost every water-caused difficulty, was full of the most astounding statements regarding the effects of a magnetic field on substances dissolved in water. However the test data show no effect in minimizing corrosion.

Another gadget, in appearance a simple cast metal fitting, was installed on the makeup water line of another cooling tower. Test coupon data for this tower and for nearby towers are given in Table 5. Again note that there was no significant protective effect. Here, too, analyses of the circulating water consistently showed low pH values and the presence of dissolved metals.

Welder and Partridge[3] have recently published an excellent review of such water-treatment gadgets.

Mechanical Factors

Corrosion control is made difficult, if not impossible, in many air-conditioning systems by the design of units, such as cooling towers or evaporative condensers, or by the design and installation of the complete system.

Materials of Construction

The importance of selection of proper materials of construction for component units is now reasonably well recognized. Many manufacturers go to extra effort to build in additional corrosion resistance by practices such as post-assembly hot dip galvanizing. But there is still an occasional slip-up.

TABLE 2—Water Compositions at Site of Three-Week Failure

	Makeup Water	Untreated Cooling Tower Water
pH	5.1	4.2
Alk (MO) as CaCO₃	5	0
Acid as CaCO₃	0	14
Chloride as Cl	2	100
Sulfate as SO₄	3	440
Iron as Fe	0	3.6
Copper as Cu	0	1.5

NOTE: All figures except pH are in ppm.

TABLE 3—Magnetic Gadget vs Inhibitor Test Coupon Data

METAL	Days Exposed	Magnetic "Gadget" Equipped Cooling Tower	Untreated Cooling Tower	Chromate Treated Cooling Tower
		CORROSION RATE, MDD		
Steel	14	130	—	—
Steel	42	84	—	—
Steel	56	63	63	1.9
Brass	56	22	20	0
Copper	56	21	12	0

TABLE 4—Water Analyses—Magnetic Gadget Equipped Cooling Tower

	Makeup Water	CIRCULATING WATER	
		5/3/56	5/17/56
pH	7.0	5.9	2.8
Alk (MO) as CaCO₃	8	6	0
Acid as CaCO₃	0	0	91
Chloride as Cl	3	4	6
Sulfate as SO₄	11	31	140
Iron as Fe	0	0.1	0.6
Copper as Cu	0	0.7	0.4
Zinc as Zn	0	1.5	9.0

NOTE: All figures except pH are in ppm.

TABLE 5—Cast Metal Gadget vs Inhibitor Test Coupon Data

Metal	Gadget Equipped Cooling Tower		Untreated Cooling Tower		Chromate Treated Cooling Tower	
	Days Exposure	Corrosion Rate, MDD	Days Exposure	Corrosion Rate, MDD	Days Exposure	Corrosion Rate, MDD
Steel	47	62	55	63	42	6.5
Steel	99	44	82	64	84	2.8
Brass	99	7	82	17	84	0
Copper	99	5.9	82	7.4	84	0
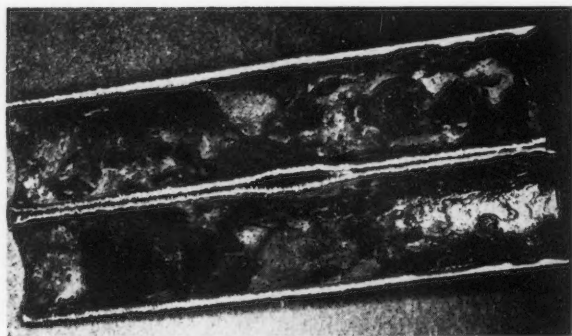
Figure 3—Copper plated steel tubing which failed in moderately corrosive circulating cooling water. Note hole. Light areas are still copper plated. Deposit is iron oxide.

Several years ago the author encountered a succession of cooling tower corrosion failures which occurred in small equipment made by a local company. These cooling towers were fabricated of aluminum without due regard to the proper alloy or surface treatment which would provide the greatest corrosion resistance.[4] Furthermore, sale of these cooling towers was promoted on the basis of corrosion resistance even though some of the construction factors were of such a nature as to promote corrosion. For example, the pans were constructed of rather light gauge aluminum sheet supported by steel angles. The drain was fastened to one of these angles. After a short period of service the bottom sheets tended to "belly" so that there was a low spot which could not possibly be drained. Evaporation of treated or untreated water concentrated dissolved salts in this depression causing serious pitting of the aluminum.

Because of the emphasis placed upon the corrosion resistance of these cooling towers, several owners did not follow the normal good practice of painting the interior of the pan. Inspection of one pan, which had been winterized by simply removing the overflow pipe so that the water drained, disclosed a black muck layer with white dots. Removal of the layer showed a deep pit beneath each dot. The dot, of course, consisted of aluminum corrosion products. This cooling tower was in an interior location but, unfortunately, the discharge duct was not louvered. With each rain the ½ inch to ¾ inch deep layer of black air-borne muck in the pan was re-wetted and provided a perfect environment for the development of oxygen concentration cells, which resulted in extensive pitting and perforation of the pan.

In this case a few additional holes in the pan were contributed by a tubular copper screen for the pump intake lying directly on the aluminum bottom sheet.

Improper selection of materials of construction also can take place during installation. A typical case involved the pitting failure of a "copper" tubing in a moderately corrosive circulating cooling water, as shown in Figure 3. A magnet revealed that the so-called "copper" tubing was actually a product made by laminating copper plated steel, and was not designed for water service.

Mechanical Design and Installation

Another built-in assistance to corrosion for some localities is the fixed area bleed collecting pan supplied in certain smaller cooling towers and evaporative condensers to assist in correcting the scaling problem prevalent over much of the country. However, in areas that have substantially non-scaling corrosive water conditions the size of the bleed built into such equipment is such that it is almost impossible to maintain adequate corrosion control treatment economically. The effect is most drastic when attempts are made to slug feed corrosion inhibitors.

The design of other cooling equipment achieves the same effect of automatic bleed by providing a pan that is too small to hold the entire volume of water that is flowing between spray heads and pan when the unit is operating. At each shut down some of the water overflows to the sewer, creating an unnecessary loss of inhibitor as well as water. This loss can be substantial in installations which cycle automatically, and may go on and off every minute or so. With this operation the water loss is greater than in equipment with a fixed-area bleed.

One make of evaporative condenser, designed in anticipation of the common failure of undersized equipment to provide enough cooling on very hot days, has been equipped with a second set of sprays directly connected with a makeup water line. When the load is too great for the equipment, the operator has only to open a valve to get added cooling by city water. This, of course, nullifies the water saving for which the equipment was put in and prevents maintenance of suitable inhibitor levels without excessive waste of chemicals.

One further observation applicable to numerous standard units used in air conditioning systems is the lack of adequate access for installing and maintaining chemical feeders, or for necessary maintenance. Without regular cleaning, air-borne dirt scrubbed out by the sprays can provide an excellent medium for development of concentration cells. It also can become the source of many mechanical troubles.

Even on specially designed equipment, consideration of operational corrosion problems at an early stage of the planning can reduce construction costs and corrosion hazards. One large cooling tower was built of aluminum because of roof loading limitations. For esthetic effect the walls were constructed of square corrugated sheet. The corrugations were placed horizontally. Unfortunately, another effect of this alignment was that air-borne dirt could settle from the circulating water on the shelves thus produced. In order to protect the siding from corrosion by the poultice effect of the moist dirt, it was necessary to coat the interior of this sheathing with a bituminous-type coating. Consideration of this factor in the planning stage would have shown the desirability of vertical alignment of the corrugations and this coating would have been unnecessary since the washing action of the water within the cooling tower would have been sufficient to keep vertical corrugations free from dirt accumulation.
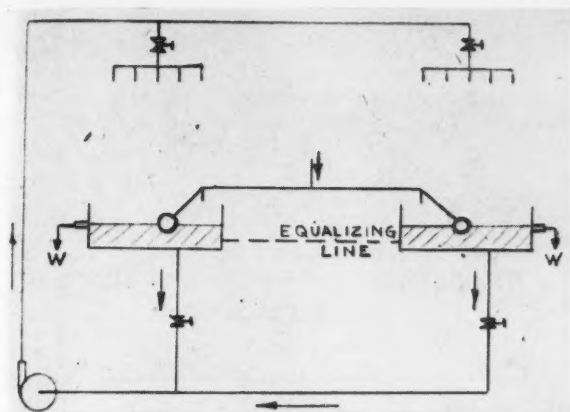
Figure 4—Twin cooling towers served by a single circulating pump wasting water and inhibitor because of hyraulic imbalance. Situation was corrected by installation of an equalizing line. The letter "W" indicates waste.

Figure 5—Imbalance of flow in twin cooling towers created by addition of refrigerant condenser drawing from pan of one tower and discharging to sprays of the second.

Figure 6—Water and inhibitor loss, created by cooling tower at lower elevation than refrigerant condensers, corrected by check valve installation.

In addition to the preceding examples of deterrents to proper corrosion control, other difficulties can be created during installation. Figures 4, 5, 6, 7 and 8 illustrate some examples. Twin cooling towers (Figure 4) served by a single circulating pump are often used. In such cases it is essential that each tower receive a balanced portion of the circulating water, for if water is withdrawn from one tower more slowly than it enters that unit from the sprays, it will overflow continuously, carrying inhibited water to waste. In the other unit the reverse action will cause the water level in the pan to drop, thus calling for additional makeup water. The pump suction connections do not necessarily serve as an equalizing line because friction differences in the pipe lines may be large compared to the head difference between the two pans. A separate equalizing line between the pans is necessary to correct the difficulty.

Even with this line present, trouble can develop (Figure 5). An additional refrigerant condenser was added to one twin tower installation equipped with an equalizer line. The circulation pump for the new condenser was piped to draw water from the pan of one tower and to discharge into the other. The equalizing line, which had performed satisfactorily before, was inadequate to handle this additional imbalance of load and the result was excessive waste of water as described above and an inability to maintain desired treatment concentrations.

Some installation errors are difficult to find. Corrosion control treatment in the cooling tower circuit of one New York office building had been under excellent control for some years when it suddenly became impossible to hold an adequate concentration of corrosion inhibitor. Investigation showed that several ice cube machines had been installed at the time the trouble was first noted. Inspection revealed copper lines running from the cooling water line to these machines, and other lines returning from each machine to the same cooling water line. Finally, the ice cube machines were disconnected and moved away from the wall in order to inspect the actual cooling water connections. Figure 8 shows the situation that was revealed. The return lines from the machines to the cooling tower circuit had never been connected and all treated cooling water entering each machine flowed to the sewer through a hidden waste connection.
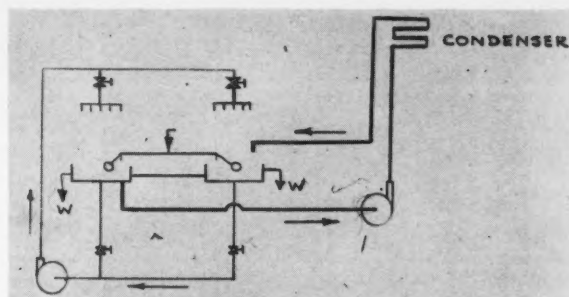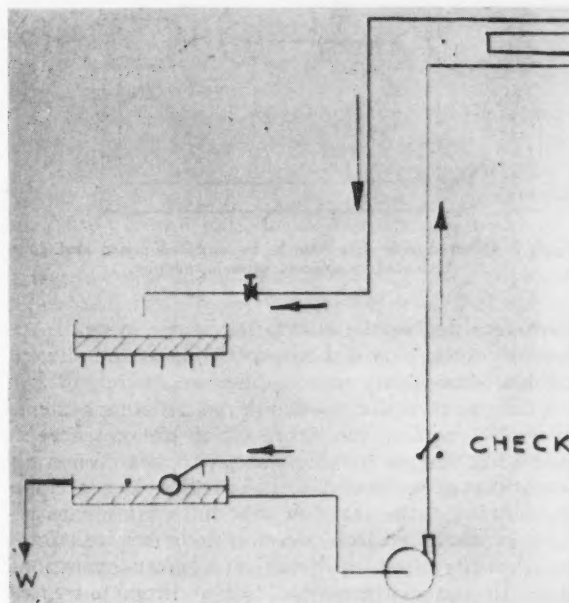
In a Philadelphia commercial building it proved virtually impossible to maintain the necessary inhibitor concentration in the cooling water of well-constructed equipment installed by a reliable contractor. The entire installation was checked without locating any apparent source of water loss. After almost a year of operation, it was accidentally discovered that a small line used for cooling an oil bearing in the compressor was discharging treated cooling tower water to a hidden drain. A check of the installation prints showed that this water was supposed to be returned to the cooling water system. Because of the height of the building, the presures were such that a heavier wall pipe would have been necessary on the discharge side of this bearing if the water
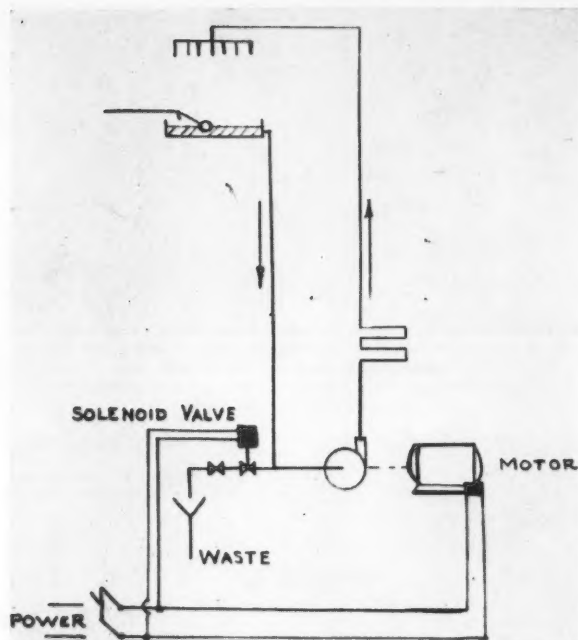
Figure 7—Treated water loss from basement bleed during shut down eliminated by solenoid valve installation.

Figure 8—Hidden waste connection causing loss of treated wate. through ice cube machines.

were returned to the circulating water system. Apparently such pipe was not available at the site, so the line was simply run to the sewer.

Effective corrosion control in recirculating systems generally requires inhibitors which are not acceptable additives for potable water supplies. When air conditioning equipment is installed in larger existing buildings, the maze of pipe lines sometimes results in unexpected cross-connections despite efforts to eliminate these connections before operations start. In one apartment building a chromate-treated cooling water system had been in use for several months when chromates suddenly appeared in the domestic water via a quick fill line which had not been used until that time. The quick fill connection was on the discharge side of the cooling water pump which operated at a pressure above the city water pressure, thus forcing chromated water into the house lines when the quick fill valve was opened.

Temporary cross-connections are sometimes set up on very hot days to supply additional water when the air conditioning equipment is undersized. In one such case (Figure 9) the appearance of a faint yellow color in the drinking water of a restaurant brought to light the fact that the building engineer was attempting to obtain additional cooling by feeding city water into the recirculating cooling water line in the basement and permitting the excess to overflow at the cooling tower on the roof. Unfortunately, this was a tall building. As a result the head pressure in the recirculating line was actually higher than the city water pressure supplying the lower floors of the building, and treated water entered the building mains.

In one sense it was fortunate that the cooling water was chromate-treated in these two cases since
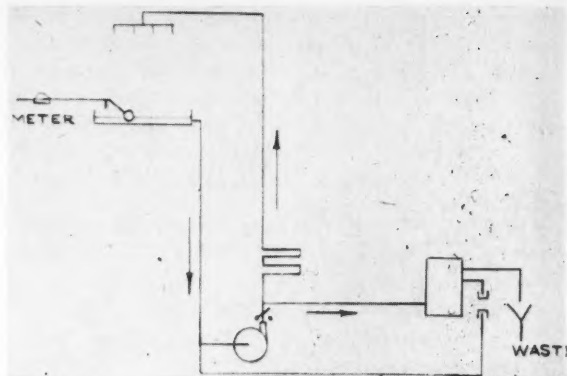
the yellow color revealed the cross-connections promptly. Corrective action therefore was taken before any serious effects developed.

These questions involving cross-connections are subject to correction by simple mechanical changes. There are other legal aspects of corrosion-control treatment that are not so readily handled. Most of these involve the question of disposal of treated waters.

Equipment Location

When air conditioning equipment is installed in older buildings there is generally the problem of squeezing it into an existing location because there is no other room available. In the case of newer buildings it is squeezed into the minimum space so as to release the greatest amount of space for productive income. Whatever the reason, the results of crowding are often damaging insofar as corrosion control is concerned. A frequently observed result of cramping is having the air washer installed with an access door so close to a wall that the door cannot be opened.

The installation of cooling towers or evaporative condensers at locations that are not readily accessible does much to discourage the maintenance man whose task it is to service the equipment. A common sight in some cities is a corner-mounted cooling tower on the roof of a building. The usual practice in this case is to place a crossflow unit with the fan on the roof side so that it is readily accessible for oiling or repair. Generally this means that the man concerned with water treatment must climb around the unit and hang by one hand several stories above the ground while sampling the water or adjusting a chemical feeder.

At other locations the only access to the cooling tower for cleaning or treatment operations is a corroded iron ladder twenty or so feet high. In one classic case a restaurant had a roof cooling tower to which access could be obtained only by clearing dirty dishes from a kitchen table, placing a step ladder on this table, climbing up, and opening an overhead roof hatch. The serviceman and all of his materials had to pass through this hatch in order to work on the cooling tower.
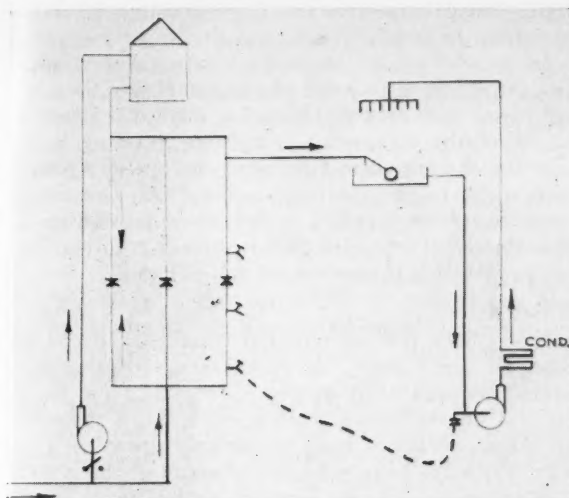
Figure 9—Cross-connection set-up by use of hose utilized in an attempt to provide additional cooling by city water.

Figure 10—Steel pipe from treated circulating water system in which cooling tower drew in exhaust air from above copper plating baths. Light areas of pipe interior are copper coated and dark areas are pitted.

TABLE 6—Effects of Cooling Tower Location on a Single Roof

	Makeup Water	CIRCULATING WATER	
		Tower A	Tower B
pH	7.1	8.3	4.3
Alk (MO) as CaCO3	63	182	0
Acid as CaCO3	0	0	2
Chloride as Cl	11	205	931
Sulfate as SO4	40	950	3500
Iron as Fe	0	0.2	250
Copper as Cu	0	0.2	0
Zinc as Zn	0	0.3	0.1

NOTE: All figures except pH are in ppm.

Another common condition resulting from installation of air conditioning equipment in existing offices and stores is a location where there is only a tiny drain or, in some cases, no drain at all. This makes it imposible to carry out properly the necessary cleaning operations or to provide a bleed if one is required.

Installation of cooling equipment without regard for the immediate surrounding environment can produce disastrous corrosion. In one southern Pennsylvania plant two cooling towers were erected at different locations on the roof of a large industrial plant. Both used the local municipal water supply for makeup. Shortly after the equipment was placed in operation, samples of the makeup and circulating waters from both cooling towers were analyzed with the results shown in Table 6. Cooling tower B was obviously in trouble. In fact, analyses of a heavy deposit removed from the circulating-water piping after several weeks of operation disclosed the presence of 35 percent copper oxide, 28 percent iron oxide and 15 percent zinc oxide.

Analysis of water from cooling tower B indicated, and a telephone call confirmed, that the tower was located close to and downwind from a smoke-stack. The stack was only about ten feet from the cooling tower and discharged at about the same elevation as the air intake louvers. It was necessary to add fifteen feet to the stack in order to eliminate most of the corrosive environment.

In another case of poor equipment location, cast iron pumps and much of the steel piping in a fairly new industrial air conditioning system were heavily copper plated and badly pitted despite apparently adequate pH and inhibitor concentrations in the circulating water. The steel pipe in Figure 10, taken from this system, shows the pitting with adjacent copper deposit. Inspection of the condenser tubes, the only copper in the system, surprisingly showed these to be in perfect condition. Investigation showed that the crossflow cooling tower was located on the roof and drew in air which was discharged from an exhaust duct about fifteen feet away. This duct drew air from immediately above copper plating tanks, apparently picking up copper-containing spray and discharging this into the cooling tower. Equipment relocation corrected this corrosion problem.

Locations in urban buildings often create hydraulic situations which are detrimental to corrosion-control treatment. One common condition (Figure 6) is the cooling tower located in the basement with one or more refrigerant condensers on higher floors. Unless check valves are installed, each time the circulation pump is shut off most of the water from the condenser and connecting piping will drain back into the tower pan and overflow. On restarting, a large volume of fresh untreated makeup water enters the system to compensate for this loss.

A similar situation is that in which an operating bleed is installed near a basement circulation pump but the cooling tower is on the roof (Figure 7). The need for a normally closed solenoid valve on the bleed line actuated by the pump electrical circuit is sometimes overlooked. Without this valve, treated water from the entire system drains through the bleed connection each time the pump is shut off.

Human Factors

In a sense it could be said that all of the factors affecting corrosion control in air-conditioning systems are human factors. The numerous difficulties encountered are invariably the result of human error in misuse of technical or economic principles. How-

ever, human factors are being considered here in a somewhat narrower sense.

Psychological Factors

On various occasions cooling-tower installations have been encountered where the discharge flows across a sidewalk or along a street before entering a sewer. Addition of almost unlimited amounts of colorless and odorless treatment chemicals to the water in such installations will cause no comment, but addition of a few hundred ppm of chromates will cause a prompt deluge of complaints from neighbors and passers-by. As a result, what should be a technical decision on the selection of a corrosion inhibitor must be modified because of the psychological effects of the inhibitor color on casual observers.

Personnel

Consulting engineers and building operating personnel have a great influence upon corrosion problems in air-conditioning systems. Among the former, a decreasing number are unfamiliar with problems resulting from recirculation of water. These engineers have practiced in the air-conditioning field for years making use of once-through cooling water and until recently have not encountered the corrosion or scaling problems which are almost inevitable with a recirculated cooling water. Their lack of familiarity with these problems reflects itself in many facets of equipment selection, location and installation. Consultation with water specialists at a very early stage in the planning of air-conditioning systems would eliminate many headaches.

Building-operating personnel are familiar with mechanical and electrical problems and can appreciate that failure to replace a frayed wire may result in injury, or that failure to replace a defective piece of mechanical equipment may result in a shut down. However, the concept of chemical treatment control, so essential to effective corrosion inhibition, is often difficult to get across. Such workers sometimes find it hard to understand that failure to maintain required concentrations of corrosion-control chemicals in a circulating water may cause just as expensive and embarrassing a failure as mechanical or electrical neglect. Through accident or otherwise, maintenance men sometimes skip treatment for a day or two and find that the equipment has not failed. This leads to a feeling that there is no great harm in neglecting water treatment, and the attitude may grow to the point where water treatment is the last item on the maintenace list and the most frequently omitted.

Smaller offices and stores are often without a regular maintenance staff or, at best, have a poor maintenance staff. In many cases these men are not informed of the necessary maintenance requirements to minimize corrosion, and in other cases they simply do not carry out the necessary operations because of other work or because they do not clearly understand the necessity for the job. For these organizations, the best solution to the maintenance problem is the employment of both mechanical-service and water-service organizations to guarantee optimum performance and life of air conditioning equipment.

In view of these conditions it is not suprising to find the common practice of supplementing the cooling tower with city water on hot days when the capacity of the equipment is fighting a losing battle with the thermometer. Generally, the operator simply adds water to the pan by use of a hose. The excess water overflows carrying with it the corrosion inhibitor. Rarely, if ever, are chemical feeds readjusted to compensate for the increased water loss.

Maintenance

It has been pointed out that certain design shortcomings can reduce the effectiveness of corrosion control by preventing proper maintenance and cleaning. Of course, there is no greater single influence on these operations than the man assigned to these jobs. With the busy schedule of many of these men, it is not surprising that so many difficulties in corrosion control start with neglect of maintenance and cleaning.

A typical example is found in cooling towers in which the water is distributed by means of perforated head pans. Failure to clean these head pans regularly results in partial clogging of the perforations by slime or air-borne dirt. The operating water level in the head pan builds up until the volume of water in this pan is larger than the lower pan will hold. Then, each time the circulating pump is stopped, the excess water draining from the head pan overflows to waste, with resultant loss of inhibitor.

Where slimogenic conditions exist, regular cleaning is critical. This is because slimicides alone are often inadequate to eliminate corrosion-promoting slime growths completely. This is particularly true in air washers because the air passing through these units goes to occupied areas of the building and, therefore, certain otherwise effective slimicides may not be used.

Poor mechanical maintenance also increases corrosive conditions. Obviously, neglect of chemical-feeder maintenance will ultimately prevent the inhibitor from entering the system. But more subtle effects of mechanical neglect may also be noted. The shaft bearings of circulating pumps of closed chilled-water systems, for example, can be the source of so much water loss when not adjusted correctly, that treated-water losses may run as high as six or eight times the system contents each month.[5]

Probably the most common mechanical-maintenance failures are in connection with the functioning of the ballcock on the makeup water line. This may leak when closed or may be set at too high a level. In either case, excessive amounts of treated water flow to the sewer making it difficult to maintain inhibitor concentration.

Treatment Control

Control is the key to corrosion-control treatment of water, and manufacturers have done an excellent job of simplifying water-testing equipment so that it can be used with reasonable accuracy by building operating personnel. But lack of adequate training frequently results in failure to appreciate and ob-

serve necessary precautions for different test procedures, and to interpret properly and apply the information furnished by the tests. The author has seen cases in which the importance of having analyses recorded on the log sheet was so firmly impressed upon the operator, and the significance of the analytical data was so lightly impressed upon him, that page after page of log book entries showed *softened* water hardnesses of 100 to 250 ppm, with no corrective action taken. In another case, a building engineer scoffed at a laboratory check analysis of his treated water because the pH shown thereon was far below the pH of *21* which he claimed was usually found by his field test. Too often, field test results are incorrect because the limited shelf life of certain reagents has been overlooked.

Poor corrosion control may result from an inadequate knowledge of sampling techniques. Regular sampling from a location near the chemical feeder discharge can result in a log book record which looks satisfactory, whereas the water in the cooling system actually is inadequately treated. In order to make operating results look good when batch feeding is employed, an occasional operator will sample batch-treated water *after* the daily addition of chemical. This results in a fine looking record, although the equipment may be in poor shape as a result.

Safety

The fact that operating personnel are generally afraid of chemicals and unaccustomed to their correct handling abets the situation. If certain building engineers known to the author were told that the white substance which they sprinkle on their breakfast eggs is really a *chemical* called sodium chloride, they probably would embark on a salt-free diet immediately. This natural antipathy toward handling of any chemical furthers the neglect of water treatment. Unfortunately, this antipathy sometimes has a very sound basis in that the operating men have not been instructed in safe handling of chemicals and, on occasion, there have been cases of chemical burns.

Legal Factors

The widespread introduction of water conservation ordinances has greatly increased corrosion problems as a result of the increased use of water-saving equipment. Air conditioning equipment which formerly operated satisfactorily for many years using a public water supply on a once-through basis has failed after a limited period of operation with recirculated water.

Once-through cooling by well waters in certain areas requires the use of recharge wells in order to conserve ground water. Many of these waters are corrosive and require treatment for the protection of existing equipment, as illustrated earlier by Figure 1. On the other hand, the water being returned to the ground may eventually enter a well serving a potable water system so that any treatment provided to the cooling water must meet requirements for potable waters.

Where recirculating equipment is used, there is still a discharge of treated water either in the form of a continuous bleed or of occasional dumping of the system contents before cleaning. Various communities have restricted such discharge either on the grounds of affecting the performance of a sewage treatment plant or on the grounds of water quantity overloading existing sewer facilities. The quality question is also raised when such wastes are discharged to streams or to dry wells which may eventually discharge into streams.

Fear of overloading sewage facilities with an excessive quantity of cooling water sometimes results from failure of the authorities to appreciate that the circulation rate of the cooling water is much higher than the rate of discharge to the sewers when water conservation equipment is used. In one community patient discussions of the quantities involved resulted in the adoption of a municipal ordinance specifically permitting the previously banned discharge of cooling waters to the sewers, provided that water conservation devices were used and provided that the total volume of water discharged to the sewers did not exceed two gallons per hour per ton of refrigeration when operating under full loading at maximum summer temperatures.

The author has encountered no bona fide case of treatment chemicals in a cooling water affecting the operation of a sewage plant. In one alleged case of such effect, bacterial action was stopped on two occasions in the sewage plant of a New Jersey community which handled wastes from several large industrial and commercial enterprises and from a relatively small number of homes. Although the sewage plant operator ascribed both stoppages to chromate-containing drainage from an industrial cooling tower, analysis of a sewage sample collected at the time of the second stoppage revealed the complete absence of chromium in any form. The trouble ultimately was shown to have resulted from dumping of a process solution containing other heavy metals into a sewage drain in one of the industrial plants just prior to each of the stoppages.

One of the primary difficulties involved in the disposal of a treated water to a public sewer or to a stream is that of finding any recognized standard for acceptable quality. With a great number of variables affecting the condition of any given stream or sewage system, and very nearly as great a number of unknowns regarding the effects of these variables, it is not surprising that the public authorities responsible for enforcing pollution regulations tend to be ultra-conservative in setting permissive limits. This results in making it extremely difficult to obtain prior approval for disposal of any treated water unless the plant involved is sufficiently large to warrant long and expensive surveys, negotiations, and waste treatment equipment costs. This is an almost impossible situation with regard to the class of equipment under discussion here.

Most existing water pollution laws are so worded that the addition of *any* quantity of *any* substance to a water provides a legal basis for forbidding discharge of the treated water to a stream or sewer. Strict enforcement of the letter of these laws would result

in the shut down of most industrial and commercial enterprises.

Until such time as improved technical information and more realistic disposal regulations permit a prompt and simple means for getting permission for disposal of treated waters from smaller installations, such treatment will be handled in a twilight zone of quasi-illegality. From the corrosion-control viewpoint this makes absence of color or turbidity, rather than effectiveness, a primary factor in inhibitor selection.

Conclusion

This paper has presented a review of the many non-chemical factors which directly or indirectly affect the efficiency of corrosion control treatment applied to cooling waters in air-conditioning systems. Economic, mechanical, human, and legal factors all influence the performance of the corrosion engineer in these installations, particularly in urban locations, requiring him to tailor the treatment chemical, method of application, and over-all operating practices to the individual area, installation, and operating personnel.

Acknowledgment

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Any discussions of this article not published above will appear in the December, 1957 issue.

Inhibiting a Cooling Water Tower System*

By F. L. WHITNEY, JR.

Introduction

THIS STUDY was initiated as a result of numerous failures of heat exchangers occurring in a plant employing recirculating cooling water tower systems. It represents an excellent cooperative effort among the power, maintenance and corrosion engineers and operating personnel to find a more economical solution to the problem. While the project was started some five years ago and although inhibition is presently considered effective, the study is being continued in order to ensure adequate protection and to evaluate new inhibitors for possible greater economy of operation. Maintaining effective inhibition at this location should result in annual savings in the neighborhood of $100,000-$150,000.

Operation Conditions

Process cooling water is provided the plant from two major recirculating tower systems. Certain towers are forced draft and others are induced draft.

In one major system the returns from the plant are collected in sumps and pumped directly back to the hot well where they are collected prior to being sent over the cooling towers and thence to the cold well.

The other major system consists mostly of overhead and underground gravity flow return lines directly to the hot well beneath the pumping station. There are several smaller systems which handle individual buildings and unit processes which were included in the study.

The initial investigation indicated that the water was extremely aggressive, producing prohibitive blockages of heat exchangers through scale deposits in addition to severe corrosion of equipment throughout both of the independent cooling tower systems. Corrosivity was determined to be the result primarily of dissolved oxygen and atmospheric contamination from various effluent gases of an acid, alkaline and organic nature released throughout the plant. A further possible source of contamination existed in the water return systems.

During this initial survey it was apparent that there were many mechanical and operating problems of waste and contamination which would prevent adequate inhibition. These difficulties would have to be rectified before any serious consideration could be given to an economic reduction of the corrosiveness of the cooling media.

The original specifications for inhibiting these systems required maintaining the pH between 6 and 6.5. This was done by adding soda ash to raise

F. L. WHITNEY, JR. is corrosion consultant for the Engineering Department, Research and Engineering Division, Monsanto Chemical Co., St. Louis. His activities include corrosion engineering and in addition he has been active in developing and participating in corrosion education activities. He obtained a BS in chemistry from Norwich University in 1930. Prior to his employment with Monsanto he was with E. I. duPont de Nemours & Co., Inc. in various capacities. Mr. Whitney served as president of NACE from March, 1955 to March, 1956.

Abstract

When recirculating cooling tower systems are used as a source of cooling water for plant operations, quality and composition of the initial and make-up water systems are not the only factors to be considered when selecting an inhibitor. Also important are the contaminating factors introduced from the atmosphere.

This paper describes a situation wherein at one plant the initial inhibitor treatment became ineffective due to expansion of plant activities and introduction of additional and greater amounts of atmospheric contamination. The value of laboratory screening tests followed by plant tests to assure proper protection are discussed. As a result of this incident the value of continuous testing in the field in a versatile and ever-growing plant is reported.

4.6.4

the pH or by adding inhibited hydrochloric acid to lower the pH. Residual phosphate concentration was to be maintained between 5 and 10 ppm by using sodium hexametaphosphate. Chlorine was added in concentrations of 0.5-2.0 ppm. Additions by the "slugging" procedure were employed. The solids content were to be maintained between 800-1000 ppm through the regulation of the water blow down and by the addition of fresh city water. These specifications were designed to provide the necessary scale, corrosion and algae control. Due to the aforementioned difficulties it was observed that in no case were any of these conditions adequately controlled.

Course Pursued in Study

To obtain an adequate yardstick by which any future corrosion prevention methods could be justified, it was necessary to determine the corrosiveness of the system under actual conditions of operation. Samples of mild steel, copper and aluminum were exposed accordingly at the top and bottom of the tower systems and in several return line locations in different operating buildings. In one or two instances samples were exposed in operating equip-
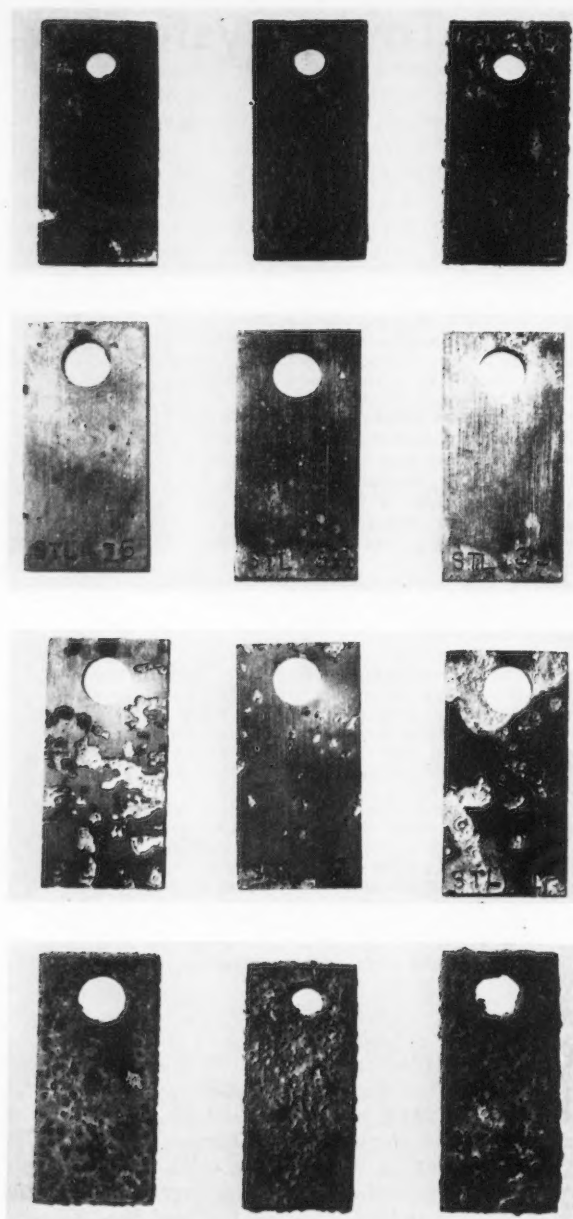
Figure 1—Mild steel test samples. Samples in top row were removed from the tower system inhibited with sodium silicate in the range of 100-150 ppm. Samples in second row from the top were obtained from the tower system which was inhibited with sodium dichromate-phosphate with residuals of 150-200 ppm and 5-10 ppm, respectively. The samples in row three show severe anodic attack which takes place when the chromate residual concentration falls below that necessary to maintain complete protection. In this instance the chromate-residual was allowed to fall below 50 ppm. The bottom row shows the condition of the samples as taken from the tower system which had been maintained at 10-15 ppm residual phosphate.

ment. The samples were installed on insulated holders and totally submerged in the cooling water streams.

The first exposure was for a period of 32 days. During this time the recommended phosphate range was not maintained. The average rate of 15 samples each in this exposure is shown in Table 1, Test A. A second test was conducted consisting of a 29 day exposure period, during which an attempt was made to maintain the phosphate content. However, due to the mechanical difficulties and operation practices, it was possible to maintain the required phosphate concentration only 58 percent of the time. The results of this test, based on an average of 15 specimens each are outlined in Table 1, Test B.

Another check test in Tower A consisting of a 40 day exposure period gave results identical to the above. Although some measure of phosphate control was maintained, it apparently had little effect on reducing corrosivity of the recirculated water.

The second major tower system was similarly tested for varying exposure periods, the average rates of which are shown in Table 1, Test C. It will be observed that the corrosion rates for steel are somewhat comparable in all tests. In all these exposures the mild steel and aluminum samples were severely cratered and pitted while the copper samples sustained slight uniform corrosion.

To compare the corrosiveness of these systems with city water, samples were exposed in the city water catch tank in one of the buildings for a period of approximately one month. The results are noted in Table 1, Test D.

A typical analysis of reclaimed water from one of the cooling water systems is shown in Table 2.

TABLE 1

	FULL TESTS			
Material	Tower A, Test A 32 Days	Tower A, Test B 29 Days	Tower B, Test C	City Water, Test D 30 Days
Mild Steel...	13 mpy	13 mpy	12 mpy	6 mpy
Copper......	1 mpy	<1 mpy	4 mpy	1 mpy
Aluminum...	1 mpy	1 mpy	10 mpy	<1 mpy

TABLE 2

Elements	Concentration, ppm
Chlorides...................	16
Oxygen (dissolved)...............	6.3
Phosphates.................	18.8 (PO$_4$)
	21.3 (NaPO$_3$)
Bicarbonates.................	Sample slightly acidic
Carbonates.................	Sample slightly acidic
Calcium.................	27.8
Total acidity.................	4.5 as CaCO$_3$
Free Mineral Acids...............	None
Free CO$_2$.................	2
pH (by glass electrode)............	7.0
Dissolved Salts.................	200 as Na$_2$SO$_4$

TABLE 3

Composition of Test Solution	Corrosion Rate, mpy	Remarks
1. Normal city water from tap (no special treatment).	16	General corrosion—no pitting. Rust held tightly to surface.
2. Reclaimed water plus 5-10 ppm phosphate. pH = 6.0-6.5 with HCl.	16	General corrosion—plus pitting. Rust loosened and thrown into solution.
3. Reclaimed water plus 40-50 ppm phosphate, 75-100 ppm chromate. pH = 5.5 to 6.0.	<1	Unaffected. Surface held high lustre.
4. Reclaimed water plus 8-10 ppm soldium silicate. pH = 6.0-6.5.	217	Spotty corrosion to surface. Pitting. Some areas holding high lustre and unaffected.
5. Reclaimed water with pH —9.5-9.0.	18	General corrosion—some pitting—loose rust coating dispersed into solution.

Depending upon mechanical operations in the plant this analysis might be typical of a recirculated water or would be concentrated (based on solids content) 4 to 5 times. Since city water by itself does not appear to be a major factor in the corrosion of these systems, analysis is not given.

Literature Search for Inhibitors

During field testing, the necessary steps by which the mechanical and operating problems could be overcome to make the use of inhibited recirculating water as economical as possible were being taken. A literature search for inhibitors which would have application in systems of these types also was undertaken. Attached is a bibliography of this survey. As a result of this preliminary survey, it was decided to conduct laboratory tests which would evaluate chromate, phosphate and silicate treatments prior to actual treatment in the field. The objective of these tests was to find an inhibitor which not only would produce a low corrosion rate (i.e., about 1 mil or less), but also would be effective in preventing pitting attack. A number of two-week exposures on mild steel samples suspended beneath the surface of the solutions, agitated by bubbling air through the liquid, were made. Typical results are shown in Table 3.

It is interesting to note that the results with steel in the laboratory test solutions containing 5-10 ppm phosphate compare rather favorably with the pre-treatment era plant tests, (see Table 1, Tests A, B, & C.) Additional laboratory tests were made at elevated temperatures and with varying concentrations. The results indicated that the most effective concentration, both from a general corrosion standpoint and to prevent pitting attack, was 75-100 ppm chromate, 40-50 ppm sodium hexametaphosphate at a pH of between 5.5 and 6.

Approval was then obtained on the basis of these data to inhibit one of the major systems. Treatment was started and coupons of mild steel were installed in 14 to 16 different locations throughout the tower system and plant equipment to check results. It became immediately apparent that additional work would have to be undertaken with the mechanical and operating end of the system in order to make the most economical use of water and to keep the treatment costs to a minimum. It was also indicated, during this period and subsequent test periods which

included not only steel but copper, aluminum and stainless steel, that it would be necessary to increase the chromate residual to 150-200 ppm to prevent anodic attack.

A typical illustration of anodic attack on steel due to insufficient chromate content is shown in Figure 1, third row of samples.[1] Anodic attack is here defined as the large shallow areas of local attack as contrasted to the small or tiny deep pits.

While consideration was being given to the problems of control and while justification for extending the treatment to other systems was being reviewed, plant management requested additional studies to obtain as efficient but more economical inhibiting treatments. Extended study also was needed because of critical shortages of sodium dichromate. These shortages dictated the advisability of suspending sodium dichromate's use as an inhibitor; consequently one system was returned to the use of phosphate and one system employed sodium silicate. Again steel samples were installed in the tower systems and in the plant to check the performance of these inhibitors. Some typical results are tabulated below in Table 4.

It will be observed that although the phosphate residual was increased to 10-15 ppm, the corrosion rate and type of attack are comparable with the results obtained from the pre-treatment era. Increasing the sodium silicate concentration to 100-150 ppm showed some improvement over the laboratory tests with 8-10 ppm but the concentration was insufficient to maintain good protection and prevent pitting. It will be observed further that the corrosion rate under actual plant conditions is higher with the 150-200 ppm of chromate than was obtained in the laboratory tests. Protection was considered essentially complete, however, since there was only minor evidence of pitting attack or anodic attack on the surface of the specimens.

Tower System Inhibited with Sodium Silicate

Typical appearance of specimens as removed after approximately two months exposure and prior to cleaning are illustrated in Figure 1. The top row of samples was removed from the tower system inhibited with sodium silicate in the range of 100-150 ppm. It will be observed that these specimens contain a hard, fairly dense coating which would adversely affect heat transfer. Beneath this coating appreciable pitting attack was sustained. The average rate of corrosion of these and other samples similarly exposed was 12 mpy for a 960 hour exposure period.

The samples in the second row from the top were obtained from the tower system which was inhibited with sodium dichromate-phosphate with residuals of 150-200 ppm and 5-10 ppm respectively. This was the treatment which was in use at the time it was decided to stop the addition of chromate as an inhibitor. A few very shallow pits will be observed on two of these specimens while one remains virtually unattacked. The depth of pitting on these samples was insignificant. The corrosion rates of these

TABLE 4

Treatment	Corrosion Rate, mpy	Appearance of Surface
Phosphate (10-15) ppm meta-phosphate residual).	15	Covered with soft, bulky coating. Cleaned sample shows severe cratering, anodic, and pitting attack.
Sodium silicate (100-150 ppm silicate residual).	12	Covered with very hard and fairly dense coating. Some evidence of anodic attack in progress.
Sodium dichromate (150-200 ppm chromate residual).	2	Very clean surface and thin highly iridescent film covering. Minor evidence of anodic attack of insignificant penetrations.
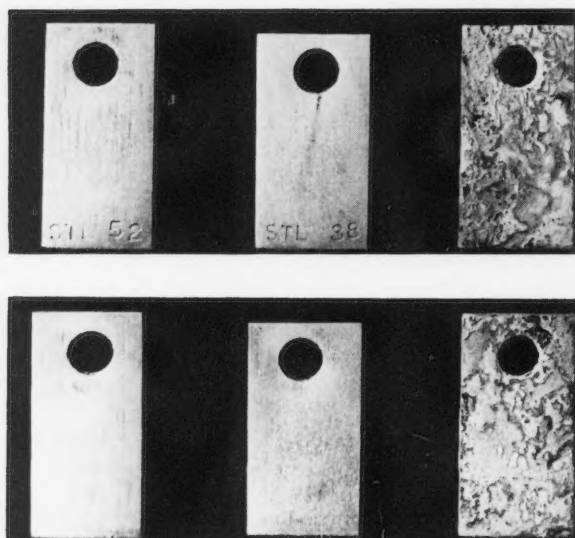
Figure 2—View of steel samples as removed before cleaning. Sample No. 52 (left) was in the solution inhibited with sodium dichromate, 175 ppm and 10 ppm phosphate. Specimen No. 38 (center) was exposed in the solution inhibited with Inhibitor A (an organic chromate containing 13 ppm residual chromate). Sample on the extreme right was exposed to plant-reclaimed water containing 15 ppm residual phosphate. Specimens in top row have front of specimen showing while bottom row shows the reverse side of the same specimens.

Figure 3—View of specimens prior to cleaning. Top row shows front side of specimens and lower row the back side of same specimens. Samples to the left were those in the phosphate treated systems while those to the right were in the system treated with Inhibitor A.
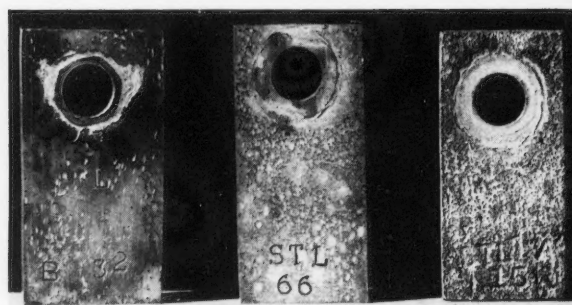
Figure 4—Steel coupons exposed for periods ranging from 218 to 349 days. Sample B-32 (left) was in Inhibitor A-flowing conditions while sample 66 (center) was in Inhibitor A-stagnant conditions. Sample 15 (right) was in the phosphate-inhibited system under stagnant conditions.

TABLE 5

Inhibitor	Chromate Concentration, ppm	pH	Cost per 1,000,000 Pounds of Water*	Corrosion Rate, mpy	Remarks
Phosphate (Plant reclaimed water)	0	6	$ 2.97	22	Severe corrosion and deposition.
A (Organic chromate)	13	6.5	11.00	0	Very slight scattered pitting.
B (Organic colloid chromate)	13	7.5	17.50	<1	Severe, local pitting.
C (Inorganic chromate)	20-40	7.4	11.20	1	Localized anodic attack.
C (Inorganic chromate)	160	7.4	55.00	0	No visible attack.
D (Phosphate chromate)	10-15	6.5	12.50	6	Severe, localized attack.
D (Phosphate chromate)	20-30	6.5	25.00	1	Severe, localized attack.
Sodium dichromate plus 10 ppm phosphate	75-100	6	12.50	<1	Slight localized attack.
Sodium dichromate plus 10 ppm phosphate	150-200	6	25.00	<1	Very slight localized attack.

* 1952 costs.

samples under this particular treatment ranged from 1-2 mpy.

The samples in the third row show severe anodic attack which takes place when the chromate residual concentration falls below that necessary to maintain complete protection. In this instance the chromate-residual was allowed to fall below 50 ppm.

The bottom row of three samples shows the condition of the samples as taken from the tower system which had been maintained at 10-15 ppm residual phosphate. The samples were covered with a fairly soft bulky coating beneath which was severe

anodic and pitting type of attack. The average corrosion rate of these and other samples exposed in this environment was 15 mpy.

Investigation of Other Inhibitors

The results of these tests, of course, clearly indicated the necessity for return to the chromate inhibitor system. However, as mentioned previously, it seemed essential to investigate other inhibitors which might be just as effective and yet use less chromate or employ other chemicals which were not on the critical list. As a result, an extension of the initial survey indicated that phosphate, inorganic chromate, organic colloid chromate, organic chromate, and organic chromate-phosphate inhibitive treatments probably would represent the field.

The problem was reviewed with water treatment specialists. Analyses were provided similar to the one shown in Table 2, and representative water samples were submitted to these specialists for additional analysis. Recommended treatment procedures and concentrations were then forthcoming which were tested in the laboratory with plant recirculated water and city water to determine the effectiveness of the treatment. These tests were run at room tem-
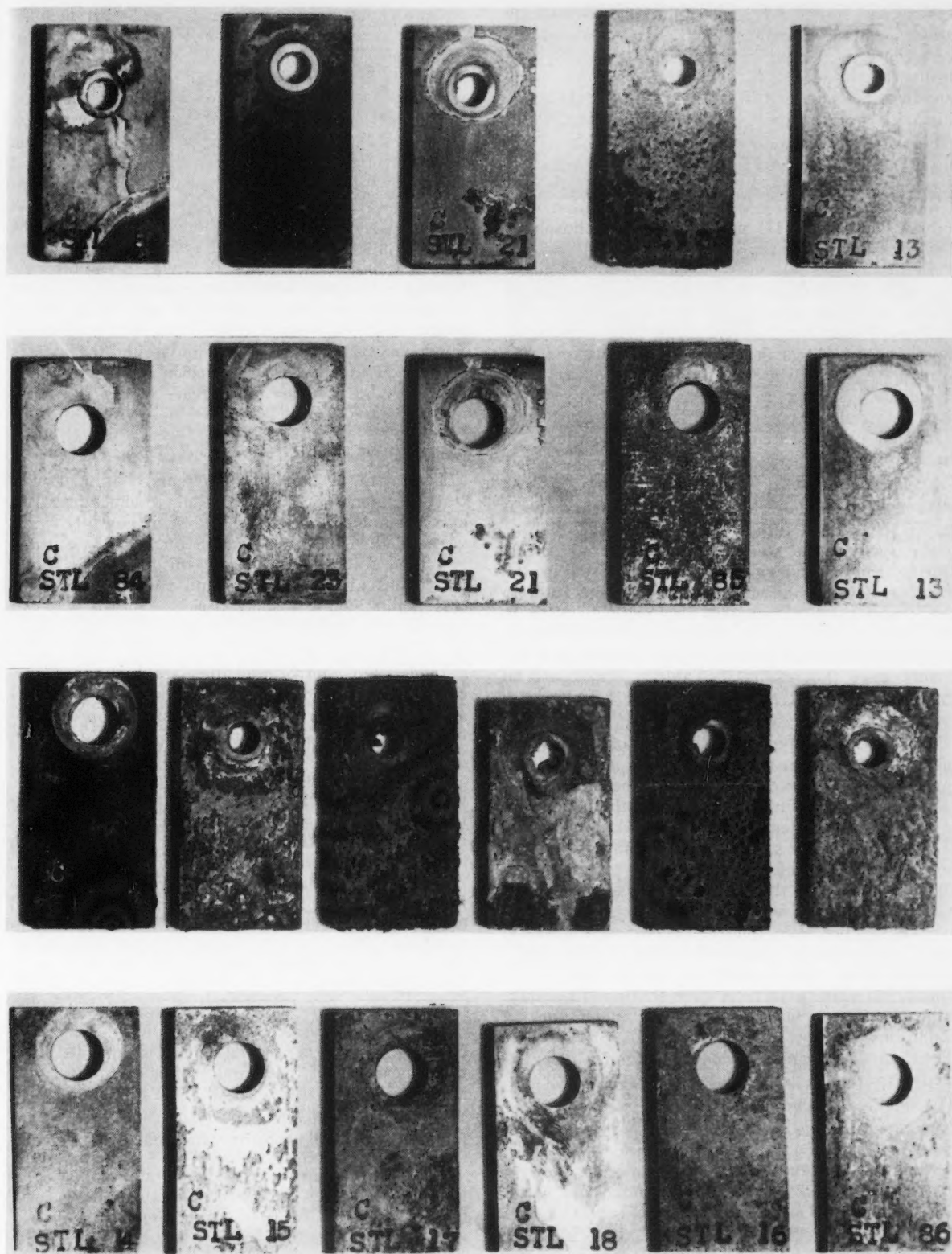
Figure 5—Various samples after approximately one month's exposure. The first and third rows reveal condition of the samples prior to cleaning, while the second and fourth rows show the appearance after cleaning. Typical exposure conditions of certain samples are: Second row: Sample 84—open tower system; Sample 23—semi-stagnant area; Sample 21—moving stream; Sample 13—phosphate treated system. Fourth row: Samples 14 and 15—phosphate treated systems; Samples 16 and 86—phosphate inhibited system where there was dilution with city water.

perature with aeration and agitation provided by bubbles of air. Treatment concentrations and pH were continuously analyzed and maintained. Typical results taken during the second month of a two-month test are shown in Table 5. Also included in this table are the costs of the various treatments.

Figure 2 shows samples as removed before cleaning comparing the best inhibitors with the plant reclaimed water containing 15 ppm residual phosphate. Sample No. 52 was in the solution inhibited with sodium dichromate, 175 ppm and 10 ppm phosphate. The specimen at the top is the front of the specimen while that at the bottom is the back of the specimen. Specimen No. 38 was exposed in the solution inhibited with Inhibitor A, an organic chromate containing 13 ppm residual chromate. The sample on the extreme right is the sample which was exposed to plant reclaimed water containing 15 ppm residual phosphate. The two samples in the chromate solution sustained no appreciable attack while that in the reclaimed water system was severely corroded.

Tests With Inhibitor A

As a result of these tests and the cost comparison shown in Table 5, Inhibitor A was selected and one tower system was so inhibited for a trial period. During this period samples were exposed in the tower system and at various points in the plant to check performance. Samples also were installed in the other tower system which remained on phosphate treatment, 15 ppm residual. A one-month exposure gave the results in Table 6. These are an average of several samples covering a one-month exposure period.

Figure 3 shows typical appearance of these specimens as taken from the systems and prior to cleaning. The samples to the left were those in the phosphate treated system, while those to the right were in the system treated with Inhibitor A. The results of these tests were sufficiently encouraging to warrant continuation of the test in this tower system and to extend it to the other major systems. Certain individual systems where wastage was high, however, could not then justify the cost of this treatment and were not so treated. When the two major tower systems were completely treated with Inhibitor A, extensive field tests were continued to determine the effectiveness of treatment under varying conditions of flow, temperature and continuity of operation. During this period of testing, which covered more than a year, it was observed that a residual chromate concentration of 13-15 ppm of Inhibitor A was too low to ensure complete protection

under all conditions. As a result, it was recommended that the treatment be increased to a residual chromate concentration of 15-20 ppm.

A question was raised during this period as to whether adequate protection was being obtained since experience showed phosphate treatment alone was not effective in stagnant areas. A comparison of the performance of Inhibitor A, both stagnant and flowing, with phosphate treatment, is shown in Figure 4. These were for exposure periods from 218 to 349 days. The rate on the steel sample in the stagnant phosphate inhibited system was ten times that of Inhibitor A. Sample B-32 was in Inhibitor A-flowing conditions, while sample 66 was in Inhibitor A-stagnant conditions. Sample 15 was in the phosphate inhibited system under stagnant conditions. Some concentration cell corrosion around the spacers and anodic attack may be noted in sample 66 which indicates the need for an increase in residual chromate.

Inadequate Control

Treatment of the major systems continued with test specimens in critical locations to check performance. Samples were removed first at monthly intervals and then the period was extended to two, three and then six months. During this period of study, careful attention to control and operating practices was maintained. In some periods control was not adequately maintained which showed up very quickly on the test coupons.

Inadequate control was due largely to the ever-changing conditions within the plant involving operating practices, process changes, expansion of facilities, and equipment shutdowns. It was apparent, however, that treatment with Inhibitor A was considerably more effective than with the phosphate treatment. Thus further consideration was entertained toward the use of this material in other systems. These systems were smaller in scope though nonetheless important from an operating standpoint. As a result of this decision, corrosion tests were made in the plant to compare an Inhibitor A-treated open tower system with an essentially closed system and one of the minor systems which continued to remain on phosphate treatment. Figure 5 shows typical samples following their removal after approximately one month exposure. The first and third rows of samples were as removed from the system before cleaning, while the second and fourth rows show the appearance of the samples after cleaning. Average corrosion rates are shown in Table 7.

Observations made as a result of this test are indicative of the problem which faces a plant in

TABLE 6

Inhibitor	Location	Corrosion Rate, mpy	Remarks
A.............	1	<1	No visible attack.
A.............	2	<1	One anodic area, remainder free from attack.
A.............	3	<1	No visible attack.
Phosphate treatment 15 ppm	4	10	Severe non-uniform attack, bulky coating.

TABLE 7

System	Corrosion Rate, mpy	Remarks
Tower system inhibitor A.......	6	Slimy deposit removed by washing.
Tower system phosphate.......	29	Hard scales, severe attack.
Closed system inhibitor A......	3	Clean surface, slight anodic attack.
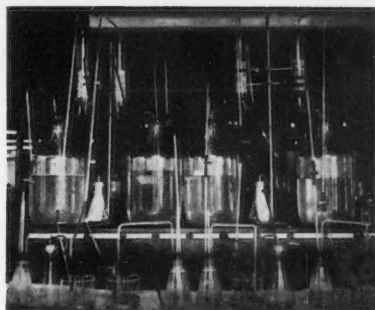
Figure 6—Laboratory apparatus used in tests to evaluate metallic phosphates.

Figure 7—Appearance of samples after tests. Top row shows front side of samples and bottom row the reverse side. Samples were exposed as follows, left to right: Sample 24—city water; Sample 25—plant recirculated water, phosphate 24 ppm residual; Sample 26—plant recirculated water treated with Inhibitor A; Sample 27—plant recirculated water inhibited with metallic phosphate, residual 24-34 ppm.

maintaining protection of inhibited cooling water systems. The closed system was protected only 68 percent of the time and subject to pitting attack the remainder of the time. It exhibited a moderate corrosion rate of 1 mpy in a moving stream (sample No. 21) and 5 mpy in a semi-stagnant area (sample No. 23). Even in this "ideal" system there is room for improvement in control.

The open tower system was protected only 45 percent of the time and exhibited a similar corrosion rate of 6 mpy, (sample 84). The phosphate treated system exhibited a *minimum* corrosion rate in the range of 15 mpy, samples 13 and 14, which is approximately three times the *maximum* experienced in either the closed or open tower systems treated with Inhibitor A. It is interesting to note in this phosphate inhibited system that where dilution with city water was experienced the corrosion rates were in the order of 26-36 mpy, (samples 17, 16 and 86). In all of the phosphate treated systems a hard scale coating was formed beneath which severe attack was observed. Attack ranged from general corrosion, anodic—sample 15, to pitting. In the systems treated with Inhibitor A there is either no scale formed or a soft slimy scale which could be readily washed off.

Use of Pictorial Methods

As was mentioned previously, this method of testing in the field not only serves as a very excellent measure toward indicating the control required, but also gives a good indication of the protection that is being obtained. The use of pictorial methods such as shown in Figure 5 serves to emphasize the importance of control to both operating and engineering personnel.

As a result of continued field testing, considerably more effort is being devoted to overcoming mechanical and operating difficulties to maintain adequate control and to extending the use of Inhibitor A treatment to the remaining systems in which there appears justification for the added expense.

Although some satisfaction has been expressed with the Inhibitor A treatment, the search continues for equally satisfactory materials which cost less. Among the more interesting materials being studied in the laboratory are the metallic phosphates. Laboratory tests are currently in progress to evaluate these materials along with the other types of in-

TABLE 8

Treatment	Exposure Period	pH	Corrosion Rate, mpy	Flow Rate, Gallons per Hour	Remarks
City water only	Four Weeks	7-8.4	7	20	Rust film on 30-40 percent of sample. Anodic attack—depth 1 mil.
Plant recirculated water, phosphate 24 ppm.	Four weeks	7-7.6	6	23	Forty percent rusted, hard scale. Severe anodic attack, depth 8 mils.
Plant recirculated water, Inhibitor A, chromate, 24 ppm.	Four weeks	7-7.6	<1	22	Slimy film easily washed off. No difference in appearance from first week.
Plant recirculated water, metallic phosphate 56-46 ppm.	One week / Two weeks	7-7.6 / 7-7.6	1 / <1	25 / 25	Slimy film, one pit in stencil mark.
Plant recirculated water, metallic phosphate 24-34 ppm.	Twelve days	7-7.6	<1	25	Slimy film easily removed. Appreciable anodic attack, depth 1½ mils, pitting 1 mil.

hibitors. The apparatus used in these tests is shown in Figure 6.

Based upon past experience with recommended treatment dosages, the program started out with a rather high residual phosphate concentration. After a two-week exposure the phosphate content was reduced approximately 50 percent and the test continued for another two weeks. The preliminary results obtained to date are shown in Table 8.

Lower Corrosion Rates

It will be observed that the corrosion rates in the city water and plant recirculated water are considerably lower than those observed in previous tests.

Inhibitor A treatment, however, checks out fairly well on these short-term tests. The metallic phosphate with a residual phosphate concentration of 56-46 ppm seems to be comparable in performance to Inhibitor A. The one pit observed in the first two weeks exposure may be due to a faulty specimen. However, anodic attack appears to be sustained when the concentration is dropped to a range of 24-34 ppm.

It is interesting to note that extrapolating the local anodic attack indicates a rate of 13 mils per year for city water, 100 mils per year for plant recirculated water inhibited with phosphate at 24 ppm, and 30-46 mils per year for metallic phosphate inhibited recirculated water, phosphate residual 24-34 ppm. With such rates of local attack it is not difficult to envision the six month to three year life obtained in various pieces of equipment.

Appearance of the samples following these tests is shown in Figure 7. Sample 24 was in city water, sample 25 in plant recirculated water, phosphate 24 ppm residual, sample 26 in plant recirculated water treated with Inhibitor A, and sample 27 in plant recirculated water inhibited with metallic phosphate, residual 24-34 ppm. Pitting and anodic attack are clearly evident on all samples except that in the Inhibitor A system.

Tests are being repeated with fresh samples in the entire system to check validity of results. Pending the outcome of these tests, which will be run for a one month period, additional tests at elevated temperatures will be undertaken to determine the temperature stability of the metallic phosphates as an inhibitor for these environments. Should this specific formulation prove unsatisfactory, it is proposed to evaluate other formulations of similar types.

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Some Experiences With Sodium Silicate
As a Corrosion Inhibitor in Industrial Cooling Waters[*]

By J. W. WOOD,[1] J. S. BEECHER[2] and P. S. LAURENCE[3]

Introduction

SODIUM SILICATE in its various forms has been used for more than thirty years to prevent corrosion of piping and metal process equipment by "aggressive" waters. J. C. Thresh[1] apparently was the first investigator to recognize the corrosion-inhibitive properties of silica. In 1922, Thresh conducted extensive tests with 48 different natural waters, mostly from sources in the English moorlands, to determine the extent to which each water would dissolve lead from lead foil. His correlated data indicated an inverse relationship between the silica content of the water and the amount of lead dissolved.

"Synthetic" waters, in which silica was introduced as sodium silicate, gave similar results. These findings prompted the use of sodium silicate for treatment of the water supply of a small municipality, in which there had been several cases of lead poisoning due to solution of lead from distribution pipes and household plumbing. The silica not only halted attack on lead, but put an end to a rusty, turbid condition in the water and stopped destruction of iron piping by corrosion.

Sodium silicate has numerous advantages which enhance its desirability as a corrosion control agent for domestic and industrial waters. A few of these are:

1. It couples ease of handling with negligible hazard to plant operators.
2. It is completely non-toxic in normal use concentrations.
3. It adds nothing to the water that is not a normal constituent of many natural waters.
4. It does not impart any taste, color or odor to the water.
5. Because of items 2, 3 and 4, the use of sodium silicate in industrial service waters creates no disposal problems.
6. It is economical (i.e., the unit cost of treatment is low).

Stericker[2] has classified both the natural and synthetic forms of water-soluble silica in the following four categories:

1. Crystalloidal silica: gives characteristic color

Abstract

The use of sodium silicate as a corrosion control agent for open-recirculating cooling water systems is discussed. Emphasis is placed on the results of tests made with low-carbon steel coupons in eight operating plants. The normal development of silica films, effect of prior corrosion and the influence of pH, water temperature and magnesium hardness are discussed.

Long-term test data indicated that crystalloidal silica is highly effective in stopping corrosion of mild steel by a wide variety of industrial cooling waters. Thirty to forty ppm of total crystalloidal silica provided adequate protection in waters containing upwards of 500 ppm of chlorides and sulfates. Magnesium hardness in concentrations above 250 ppm as $CaCO_3$ was found to greatly reduce the inhibitive action.   **5.8.2**

reaction with ammonium molybdate and has marked corrosion-inhibitive properties.

2. Stable hydrated colloidal silica: does not give color test with molybdate and is a better inhibitor than crystalloidal.

3. Unstable hydrated colloidal silica: does not give color reaction and is a poor corrosion inhibitor. Unlike crystalloidal and stable hydrated forms, this material may form gels or gelatinous precipitates on standing.

4. Unhydrated silica: does not give color reaction and does not form gels but may settle out on standing. It has no influence on corrosion.

The discussion to follow will be concerned mainly with the first form (i.e., ionic or crystalloidal silica).

Scope

Experiences with sodium silicate as a corrosion control agent for open-recirculating cooling water systems will be described in the paragraphs to follow. More particularly, the results of tests made for evaluation of silica treatment in several operating plants will be reported. These tests were not controlled experiments. Rather they were long-term studies designed to determine the degree of protection afforded by silica treatment of the various waters. In some cases the treatment proved unsatisfactory. It is hoped that by a rough correlation of the data describing the water in each system, and those showing the extent of attack on the test specimens, it will be possible to draw a few conclusions regarding the effectiveness of silica treatment and the conditions which may limit its applicability.

The data to be discussed were obtained from study of coupon-type metal specimens exposed in several

	Plant 1	Plant 2
pH	7.2	7.3
Total alkalinity¹	28 ppm	33 ppm
Calcium¹	450	390
Magnesium¹	67	52
Chloride as Cl	65	47
Sulfate as SO₄	550	440
Silica as SiO₂	35	22
Temperature	84 F	85 F

¹As parts per million expressed as CaCO₃
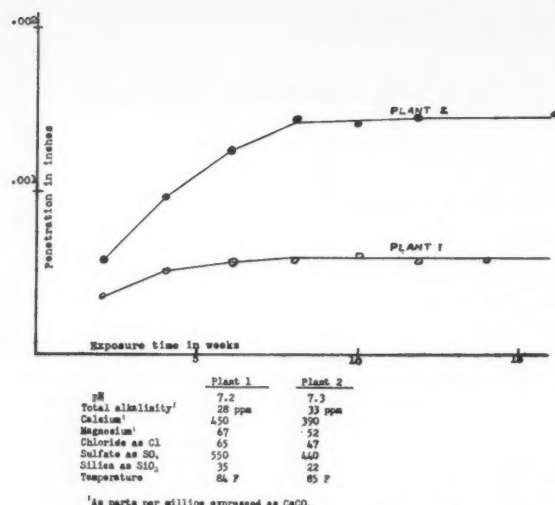
Figure 1—Effect of silica concentration on penetration depth. Penetration values are computed from weight loss data.

Figure 2—Maximum penetration depth for coupons exposed in Plants 1 and 2 (microscopic determinations.) Plant 1 had 35 ppm SiO₂ and Plant 2 had 22 ppm SiO₂. Complete data are shown in Figure 1.

different industrial cooling systems. It will, of course, be understood that data from test specimens installed in an operating system should not be considered to be a precise measure of the extent of corrosive attack on the component metal parts of that system.

This last statement is especially true when the purpose of the tests is to obtain an indication of the effectiveness of a corrosion control agent in the system under study. Except in the case of new plant equipment, the "corrosion history" of the equipment before conditions were changed by introduction of treatment, is likely to affect the nature of the reactions between the structural metal and the treated water. On the other hand, the test specimens, which have had a different "corrosion history" (usually none at all), probably will react in a much different manner—at least during the initial period of exposure. In short, the system "old equipment plus treated water" differs enough from the system "new specimens plus treated water" so that the actual corrosion rates in the two systems may vary considerably. In most cases, the difference will decrease as the duration of the test period increases.

The preceding comments indicate, in a general way, the limitations which must be imposed on interpretation of test data. With these qualifying considerations, specimen test data may be regarded as highly indicative of the type and severity of corrosion in process equipment. For example, if a coupon specimen shows mild, uniform general attack, one would not expect to find extensive active pitting in pipe lines. Again, if a number of coupons are installed at the same time and removed at successive
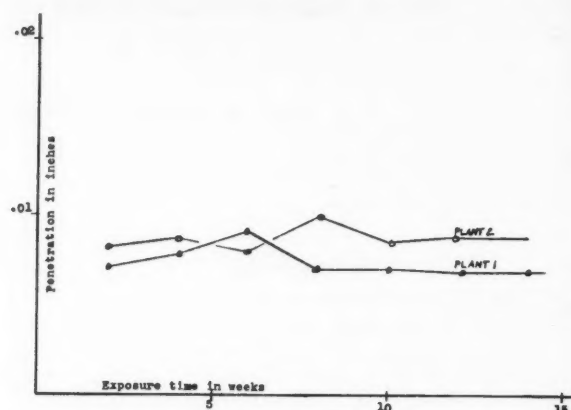
TABLE 1—Analysis of Steel Used for Test Coupons

	ELEMENT							
	C	Mn	P	S	Si	Cu	Ni	Cr
Composition, Percent	0.05	0.32	0.006	0.034	0.004	0.035	0.02	0.02

intervals, a continuing progressive increase in percent weight loss indicates active corrosion of the equipment.

It has been the authors' experience that attack on test specimens, as measured by the usual methods, is usually more severe than that revealed by examination of the actual equipment. This is probably due in large part to the fact that specimen surfaces are especially prepared so that there will be no "accidental" factors which will interfere with normal corrosion reactions.

Treatment of Test Specimens

Test-coupon studies were made in eight different open-recirculating cooling water systems. Compositions, temperatures and flow rates of the waters in these plants varied considerably. However, all systems had one common characteristic: prior to introduction of silica treatment, each had a history of severe pitting of steel parts. None of the systems were exposed to unusual atmospheric contaminants.

All coupons were sheared from a single sheet of steel. The analysis of the metal is given in Table 1. This material was selected because it is a typical low-carbon steel, resembling the low-carbon components of all systems in which the tests were carried out.

At each test site, a considerable number of 1 inch by 4 inches by 0.0625 inch specimens were installed at the same time. Specimens were removed in pairs for study and evaluation at successive intervals (two to four weeks) during the test periods. For the most part, the specimens were suspended in open parts of the systems, as in tower basins or hotwells, in areas where continuous motion of the water was assured. In some instances, plastic holders mounted on pipe plugs were used to support coupons rigidly inside large pipe lines. In all cases, care was taken

to prevent contact of the specimens with each other, or with tank or pipe walls.

The only preparation given the specimens prior to the initial weighing was removal of surface dust by rubbing with a soft cloth, followed by de-greasing in acetone and ethyl ether. In one test, a few specimens were allowed to rust after weighing and before exposure. This was done in an attempt to simulate conditions that might exist in a system that had been in operation for some time before silica treatment was begun. In all other cases, precautions were taken to prevent corrosion of the coupons before installation.

In assessing the effects of exposure on the metal specimens, the following procedure was followed:

1. After preliminary examination with a hand lens, any surface deposits were removed with a plastic scraper.

2. The metal surfaces were examined with a lens after scraping as was the material that was removed. If any unusual condition were noted, a microscopic examination was made.

3. The coupons were cleaned of adherent deposits with dilute inhibited acetic acid, according to the procedure outlined under ASTM designation D935-49.

4. After cleaning, the specimens were dried, weighed, and given a thorough visual and microscopic examination.

5. Interpretation of data from these studies is based on changes, or lack of change, in the measurements made on successive specimens from each test series.

It is common practice to report data from corrosion tests in the form of "corrosion rates," which are calculated from the specimen weight loss, the time of exposure, and the area or thickness of the specimen. When the data have been so treated, the reported figures must be interpreted something as follows: "During an exposure period of x weeks, the average corrosion rate for these specimens was x inches per year." In this paper, the penetration (computed from weight loss data) that was determined for each set of coupons at the end of the exposure period is reported.

Nature of Environmental Waters

Table 2 gives the analysis of the circulating water in each plant or system studied. Deviations from the

values listed, during the test periods, were minor. In most systems, dosage of sodium silicate was controlled to maintain a concentration of 35 ± 5 parts per million total crystalloidal silica. It was not practicable to attempt closer control, because of fluctuations in silica content of the makeup waters. In a few cases, different control limits were used. Also, in most cases, sulfuric acid was used to maintain pH at approximately 7. The concentrations of other constituents were held nearly constant by controlled bleedoff.

Silica was fed continuously to all systems as an aqueous solution of sodium silicate. Feed rate was increased or decreased as indicated by results of daily control tests. In all cases, the control test used was the colorimetric "reduced molybdate" method.

The silica content of the water was maintained at approximately 70 ppm for several weeks at the start of the program. This accelerates the initial formation of protective films. All tests discussed in this paper were begun after this starting period, when silica dosage had been dropped to "normal" values.

Normal Development of Silica Films

Lehrman and Shuldener[3] have demonstrated that silica is not deposited from water on clean iron or steel surfaces. It is necessary first that a layer of iron oxide be present before the protective silica film is formed. Vail[4] cited Texter[5] and Speller[6] to the effect that maximum protection by silica is not obtained until 22 days or more after treatment is started. For these reasons, it is to be expected that when tests are made with clean specimens, some corrosion or rusting must take place before any inhibitive action begins. This should be reflected in relatively high initial weight losses.

The data from the present studies appear to be consistent with these views. For example, the curves of Figure 1 show a marked (but not serious) loss of metal after only two weeks exposure. As the curves indicate, corrosion continued at a steadily diminishing rate, for another three to five weeks.

It will be noted that the waters in Plants 1 and 2 are substantially alike. It was not surprising, then, that the earlier specimens from each test series were very similar in appearance; they showed numerous very small pits, capped by small rounded tubercles:. In the case of Plant 2, where the silica content of the water was lower, pitting continued for an appreciably longer time than in Plant 1. The curves reflect this clearly. Although they have the same general shape, the curve for Plant 2 levels out (indicating that corrosion was halted) at a point above and to the right of the corresponding point for Plant 1. Obviously, in Plant 2, a longer time was required for development of the protective film, with resulting greater loss of metal.

It is somewhat surprising that such a relatively small absolute difference in silica concentration (13 ppm average) should have so marked an effect on the rate of

TABLE 2—Partial Analyses of Waters in Which Coupons Were Exposed[1]

	Plant 1	Plant 2	Plant 3	Plant 4a	Plant 4b[2]	Plant 5	Plant 6	Plant 7	Plant 8
pH	7.2	7.3	7.4	8.6	7.0	7.6	6.6	7.6	7.0
Total Alkalinity[3]	28	33	54	380	21	158	24	114	52
Total Hardness[3]	518	442	585	280	270	850	786	530	415
Calcium[3]	450	390	440	210	194	460	530	444	320[3]
Magnesium[3]	68	52	145	70	76	390	256	86	95
Chloride as Cl	65	47	186	43	45	760	480	610	108
Sulfate as SO4	550	440	460	20	350	690	520	290	210
Silica as SiO2	35	22	32	31	31	30	45	33	38
Temperature:									
Tower Basin	84 F	85 F	70 F	82 F	82 F	78 F	81 F	78 F	72 F
Hot Well	104 F	110 F	100 F	98 F	98 F	91 F	97 F	95 F	92 F

[1] Values in parts per million.
[2] Water from Plant 4 with acid treatment.
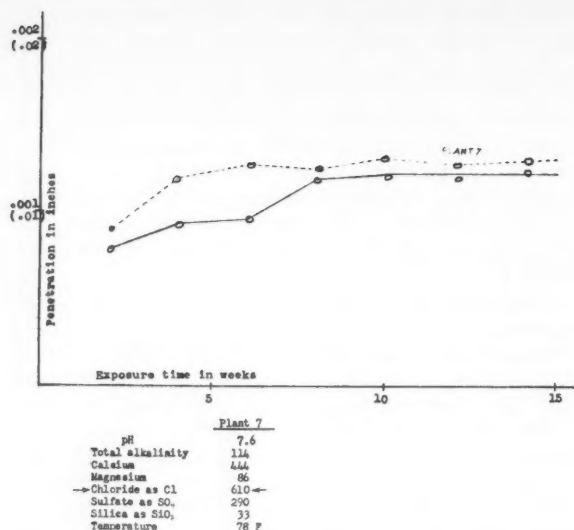[3] Expressed as CaCO₃.

Figure 3—Typical time-penetration curves for long-term corrosion tests. Numbers in parentheses on penetration depth scale are maximum depths determined microscopically.

Figure 4—Effect of high pH on penetration depth.

film formation. However, the results shown here have been confirmed by tests in other plants, as well as in the research laboratory. The fact that the times required to develop substantially complete protection in these two plants were in almost exact inverse ratio to the silica contents of the two waters, is probably coincidental.

The "penetration" values shown in Figure 1 were computed from weight-loss data. Figure 2 shows the actual maximum depths to which corrosion had penetrated, determined by measurements with a calibrated microscope. Comparison of Figures 1 and 2 reveals that there was no significant change in actual penetration depth after two to four weeks, although weight loss determinations showed that mild corrosive attack continued several weeks longer.

The appearance of successive specimens in each group provided an explanation for the seeming discrepancy between these two sets of curves. The "earlier" coupons displayed a moderate number of narrow and medium pits, with width/depth ratios of 0.5 to 2.0. Later specimens were characterized by a few irregular areas of slight to moderate semi-local corrosion, apparently the result of widening and coalescence of the original pits.

It is significant that after the initial pitting, and before corrosion was entirely stopped, the corroded areas widened without becoming any deeper. Judging from the previous corrosion history of these systems, the pits would have become progressively deeper if the inhibitor had not been present.

Figure 3 shows results in still another plant where the water differs appreciably from the first two. Penetration computed from weight losses and maximum penetration determined by direct measurement, are shown together for convenience; the latter values are represented by the broken line.

The data presented in Figure 3 are included be-

cause the chloride content of the water in Plant 7 was fairly high. It is well known that high chloride concentrations usually aggravate pitting. Uhlig[7] has discussed the reasons for this, and Eldridge and Warner[8] have pointed out that many inhibitors are less effective in high chloride waters. The fact that corrosion in this system was not more intense than in Plants 1 and 2, is in agreement with Stericker's observation[9] that the protection afforded by adequate silicate treatment is not affected by high chlorides.
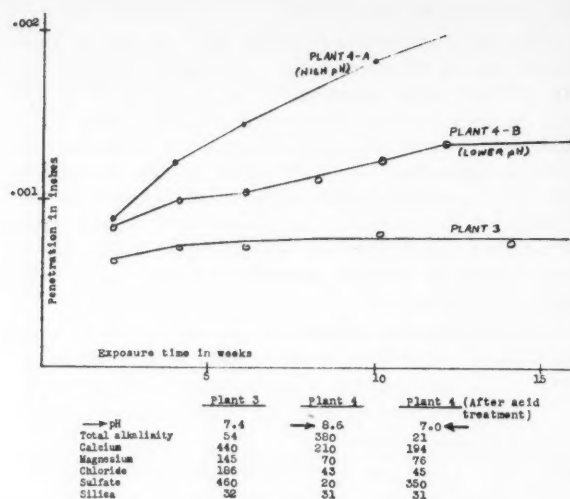
These curves resemble those of Figures 1 and 2 to a substantial degree. Curves of these general forms are regarded as typical for mild-steel specimens in water treated with sodium silicate, under suitable conditions. Some factors will be presented which apparently interfere with the silica-inhibition mechanism, producing results which do not follow this typical pattern.

Influence of pH

The effect of high pH on the inhibitive properties of silicates is demonstrated by Figure 4. Here, two sets of data obtained in the same plant under different conditions are presented for contrast. Coupon tests were started in Plant 4 shortly after silica treatment was begun; at that time, no acid was being added to the water, and the pH was about 8.6. When test results (curve A) indicated that the corrosion rate was not decreasing according to the typical pattern, chemical pH control was introduced. Sulfuric acid was used to lower the pH of the circulating water to 7.0. After this adjustment had been made, a new test series was started. Results obtained at this lower pH level conformed to the normal pattern, as is shown by curve B.

Although the acid treatment may have converted some of the crystalloidal silica, which was being fed, to a colloidal form, this was not reflected in control

Figure 5—Comparison of test results at different temperatures.

pH	Plant 2	Plant 8	
pH	7.3	7.0	
Total Alkalinity	33	52	
Calcium	390	320	Note: Analyses are
Magnesium	52	95	of samples
Chloride	47	108	taken from
Sulfate	440	210	tower basin
Silica	22	38	outlet
Basin Temperature	85 F	72 F	
Hotwell Temperature	110 F	92 F	

test results (since the test used determined only crystalloidal silica). It is possible that such a conversion was in part responsible for the improved results obtained after acid treatment was started.

Data from still another plant are represented by the third (lowest) curve of Figure 4. This very flat curve is included for comparison with the other two. The conclusion which may be drawn from Figure 4 is that at a relatively high pH, silica treatment did little to check corrosion in Plant 4. It can be seen however, that with proper pH control, corrosive attack was reduced to the extent that test results approached the nearly ideal results obtained in Plant 3.

The influence of pH on protection by soluble silicates, suggested by these data, has been noted by Stericker.

Influence of Water Temperature

Comparison of results obtained in different parts of two systems, is presented in Figure 5. In this chart, the broken lines represent penetration values calculated from weight-loss data, for specimens exposed in the hotwells of the two systems; the solid lines show corresponding data for specimens installed in the cooli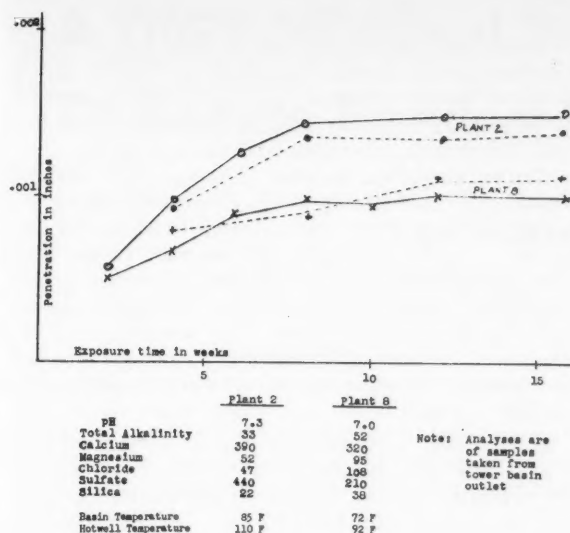ng tower basins during the same period. In general, it has been found that temperatures up to 110 F do not affect corrosion rates in silicate treated waters. These data provide direct evidence to the same effect.

Inspection of water-side surfaces of heat-exchange equipment in systems where silica-treated cooling water is used, has satisfied the authors that silicates inhibit corrosion effectively at temperatures ranging from 160 to 190 F. No coupon data are presented from such high-temperature zones in any of these plants where these studies were made, because there was no satisfactory way of installing coupons inside heat-exchange tube bundles or condenser jackets.

pH	Plant 3	Plant 5	Plant 6
pH	7.4	7.6	6.6
Total Alkalinity	54	158	24
Calcium	440	460	550
Magnesium	145	390	256
Chloride	186	760	480
Sulfate	460	690	520
Silica	32	30	45
Temperature	85 F	81F	92 F
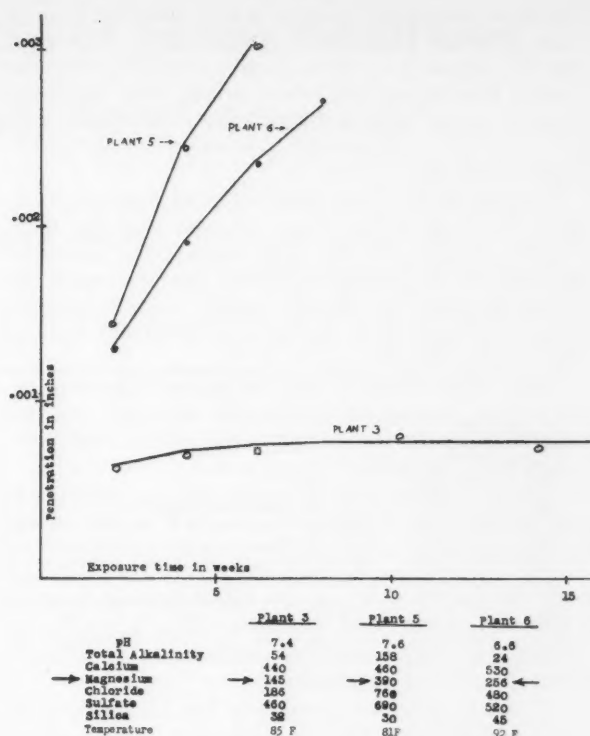
Figure 6—Effect of magnesium content on penetration depth.
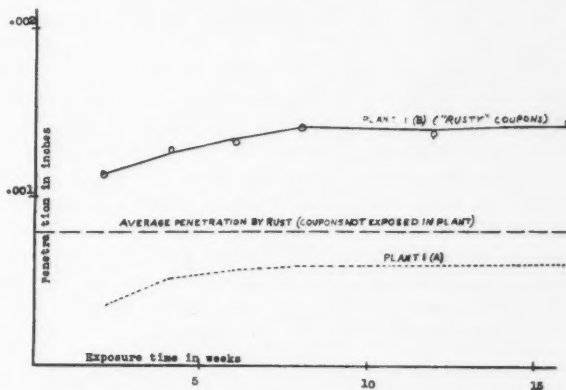
Figure 7—Test results with rusted specimens. Analytical data for Plant 1 are shown in Figure 1.

Influence of Magnesium Hardness

Test data from three plants in which the magnesium content of the water was appreciable are plotted in Figure 6.

In Plants 5 and 6, the coupons showed severe pitting. Unlike the results in the systems just discussed, microscopic measurements on successive coupons showed that these pits became deeper as exposure time lengthened. Since it was obvious that silicate treatment was not operating "according to form" another sort of corrosion control treatment was adopted in these plants.

All available information on operating conditions

in these two plants was studied, to determine which factors might affect either corrosivity of the waters or the behavior of silica. Water analyses, temperatures, flow rates and other details were reviewed and compared with corresponding data from plants in which silica treatment had been successful in halting corrosion.

One detail in which these systems differed markedly from the other plants studied was the magnesium content of the two waters. For example, except for magnesium hardness, the analytical and operating data for Plants 3 and 7 exhibit, between them, characteristics similar to all pertinent features of Plants 5 and 6.

Data from Plant 3 are repeated in Figure 6, because the magnesium hardness of the water was the highest among the plants where silica treatment showed good results.

From consideration of these factors, particularly of the data set forth in Figure 6, it is tentatively concluded that corrosion by waters containing 250 ppm or more of magnesium hardness (expressed as calcium carbonate) can not be countered successfully by addition of crystalloidal silica. It would appear, however, that water containing up to 150 ppm may be treated successfully.

These conclusions apparently are contrary to the findings of Vail[10] who, in discussing the use of sodium silicate to prevent corrosion by brines, states that relatively large quantities of calcium and magnesium salts in the brine, though they react with the silicate, do not prevent deposition of the protective film.

In considering possible explanations for this observed — or better, deduced—effect of magnesium, it was necessary to discard the patent suggestion that precipitation of silica as magnesium silicate might be the cause. In the first place, although there may have been some precipitation, there was no evidence of deposition on heat-exchange surfaces. Secondly, the water analyses showed that there was as much or more silica in solution as was present in the systems where this treatment did stop corrosion. Two tentative hypotheses are suggested:

1. Formation of non-ionized soluble magnesium-silica compounds, which would render silicate ions unavailable for adsorption on the iron-oxide film.

2. Adsorption of silica on the metal or metal-oxide surface in the normal manner, followed by reaction of magnesium with such adsorbed silica—thus altering the chemical structure of the silica film and destroying its protective properties.

These are merely speculative thoughts; there is at present no evidence, such as analytical or X-ray diffraction data, which might either substantiate or disprove them. Upon consideration of Vail's experiences, the authors are inclined to believe that this effect of magnesium is peculiar to systems in which most of the silica is in the crystalloidal form.

Effect of Prior Corrosion

Tests with specimens which had rusted before exposure in the system were made in Plant 1. Figure 7 shows results of these tests, in comparison with those of simultaneous tests using "clean" coupons (the latter data are repeated from Figure 1.)

Before exposure, several coupons were abraded lightly with fine emery cloth, de-greased, dried and weighed. They were then allowed to stand for two weeks in a warm, humid atmosphere (New York City in midsummer). Six of these coupons, picked at random, were acid-cleaned in the usual manner, and weighed to determine the amount of metal destroyed by rusting. The average rust—penetration of these specimens is indicated by the straight broken line in Figure 7.

It is readily apparent that the data obtained with the rusted coupons follow the pattern typical for silica-treated waters. In fact, if the penetration values shown are corrected for the initial metal loss caused by rusting, the two curves shown in Figure 7 will very nearly coincide. This is of considerable importance, because it indicates that silica may be used to stop corrosion after attack has started. It is not surprising that such results were obtained; actually they were expected, in view of the fact that in all systems studied the clean coupons were slightly corroded during the earlier part of the exposure period.

Conclusions

Qualitative and quantitative data from long-term tests indicate that crystalloidal silica is highly effective in stopping corrosion of mild steel by a wide variety of industrial cooling waters. Thirty to forty ppm of total crystalloidal silica provide adequate protection in waters containing upwards of 500 ppm of chlorides and sulfates. pH values of 8.6 and higher have an adverse effect, which may be corrected by judicious use of mineral acids, properly controlled. Magnesium hardness, in concentration above 250 ppm as $CaCO_3$ greatly reduces the inhibitive action. Before a protective film can be developed, it is necessary to have an initial coating of iron oxide; this is often advantageous, since it indicates that sodium silicate will be effective in systems in which corrosion is active prior to application of treatment.

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A Thermochemical Study of Some Additives To Reduce Residual Fuel Ash Corrosion*

By W. E. YOUNG and A. E. HERSHEY

Introduction

THE ABILITY of the industrial gas turbine to compete successfully with other forms of power generating equipment where inexpensive or waste gaseous fuels are available has been demonstrated satisfactorily. However, where liquid fuels must be used, the competitive position of the gas turbine depends to a great extent on its ability to operate on the lower grades of residual fuel oil. It is true that for power requirements less than 50,000 kw where mobility and rapid load variation are of primary importance, a gas turbine burning distillate fuel oil may be superior to a steam turbine plant or a diesel engine. For most applications, however, the gas turbine must be able to operate with fuel costing less than half the price of diesel fuel if it is to be considered for use.

Unfortunately the corrosivity of the products of combustion of certain residual fuels at elevated temperatures has presented a serious problem. The two most objectionable elements in the combustion ash are vanadium, in the form of vanadium pentoxide (V_2O_5), and sodium sulfate (Na_2SO_4). When both are present, a vanadium-sodium complex may be the cause of the corrosion. The sodium may occur naturally in the fuel, or it may have been introduced as a contaminant (usually in the form of sodium chloride). It can be removed, by a process of water washing, settling, or centrifuging, but since this will undoubtedly increase the fuel costs, it would be preferable to burn the fuel without such treatment.

The vanadium, on the other hand, is in the form of a very complex, oil soluble compound, a porphyrin, and since it is dissolved in the oil and not associated with solid material in suspension, it can be removed only with extreme difficulty. There are then two alternatives: either nozzle and blade materials must be found which are resistant to the corrosive attack, or fuel additives must be used to render the combustion products non-corrosive. The results of investigations of this form of corrosion on numerous available refractory materials[1,2,3] indicate that the first method is not likely to yield a satisfactory solution, at least in a reasonable time. Therefore attention has been turned to the discovery of fuel additives which will effectively inhibit the corrosion and which can be employed without too much difficulty or excessive increase in fuel cost.

W. E. YOUNG is research engineer with Westinghouse Research Laboratories, Pittsburgh, Pa., where he is engaged in combustion and thermodynamic research for industrial gas turbines. He has a BS in mechanical engineering from the University of Vermont (1941), and a PhD (1956) in mechanical engineering from the University of Pittsburgh, where he is a lecturer. He is a member of ASME and NACE.

A. E. HERSHEY is advisory engineer, Westinghouse Research Laboratories, Pittsburgh, Pa., where he is engaged in combustion and thermodynamic research and development for industrial gas turbines. From 1926 to 1942 he was with the Engineering Experiment Station, University of Illinois. He has a BS in mechanical engineering, Carnegie Institute of Technology (1922), and an MS (1926) and PhD (1941) mechanical engineering, University of Illinois.

Abstract

Based on the premise that liquid fuel-ash components are associated with the "catastrophic" attack on refractory alloys, a theoretical study has been made of mixtures of vanadium pentoxide and sodium sulfate with various metallic oxides and sulfates. The thermal stabilities of the sulfates were then investigated. It was concluded that the oxides of calcium, magnesium, and aluminum should be effective if they could be preserved in the oxide form. However, it was shown that the sulfate would in general be the stable form, particularly at gas turbine operating pressures. Such sulfates are not effective additives and may, in fact, be deposit forming. The additive with the most promise was found to be an aluminum compound. Its sulfate, even if initially formed, should revert almost entirely to the oxide at 800 C for atmospheric conditions and 920 C at five atmospheres. Some of these conclusions have been confirmed by full scale tests on turbines, but additional laboratory testing and actual operation are necessary to verify them completely. More extensive and accurate thermochemical data would contribute to the validity of the calculated results. 3.5.9

Many compounds of vanadium may be formed during combustion, but with the exception of V_2O_5, which melts at 670 C, these either decompose or have melting temperatures close to 2000 C. Likewise,

Figure 1—Ash fusion apparatus.

(1) Original sample
(2) Sintering
(3) First bubbles
(4) Initial melting
(5) Complete melting
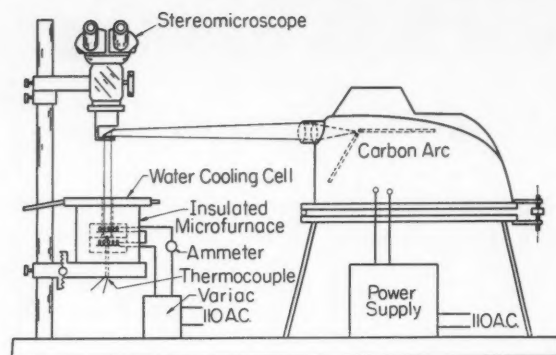
0   Scale (in.)   .25

Figure 2—Phases observed during an ash fusion test.

the stable compound of sodium which probably will be formed is the sulfate, Na_2SO_4, which melts at 890 C. Convincing evidence has been accumulated which indicates that, whatever the precise mechanism of corrosion may be when vanadium and sodium compounds are present, "catastrophic" attack is nearly always associated with the presence of a liquid-ash phase which fluxes off the protective oxide coating normally formed on refractory alloys.

If the only function of a fuel additive is to raise the melting point of the fuel ash, the importance of detailed information regarding the fusion characteristics of fuel-additive mixtures is evident. In order to investigate this aspect of the corrosion problem the micro-fusion apparatus shown in Figure 1 was developed in 1954. Since that time the fusion characteristics of many fuel ashes and ash-additive mixtures have been studied.[4] Four distinct phases of the melting process are usually observed and these may be defined as:

(a) The sintering point

(b) The appearance of the first liquid bubbles

(c) The initial melting point

(d) The final melting point

Photographs of a typical fuel ash in each of these phases are shown in Figure 2.

The micro-fusion apparatus proved to be useful as a rapid and convenient means for evaluating fuel additives. However, early attempts to find a satisfactory additive for a fuel with a high sodium concentration, showed that what was really required was a fairly complete set of phase diagrams of binary mixtures for the different ash constituents and various proposed additives. As may be seen from the melting point curves for Na_2SO_4 - $MgSO_4$ mixtures in Figure 4, when these two sulfates were mixed with a magnesium-sodium ratio of 0.5 the temperature of the complete melting point was lower than that of either of the pure compounds. In a few instances such diagrams were found in the literature,[5] but for many of the more promising additives no diagrams were available. However, using thermochemical data it is possible to calculate ideal melting point curves for binary mixtures which may be of some use in selecting ranges of fuel-additive com-
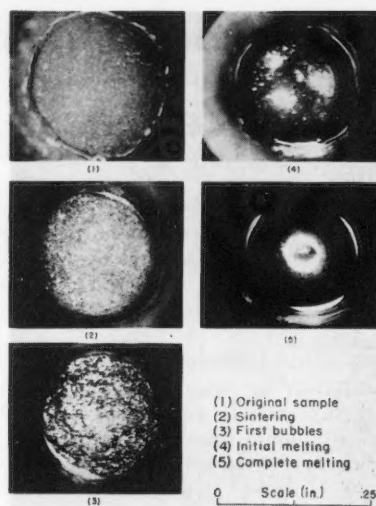
positions which should result in solid ash products at turbine operating temperatures.

Calculated Freezing Point Curves

Theoretical melting point curves for binary systems can be computed from the thermodynamic properties of the components. Such a computation is based on the lowering of the freezing point of a solution as known amounts of solute are added to the solvent. Rossini[6] considers the case of equilibrium between a pure solid substance and an ideal liquid solution containing the pure solid in dissolved form with the following simplifying assumptions:

(a) The mixtures are true binaries.

(b) They behave as ideal solutions over the entire range of composition.

(c) The solutes are completely soluble in the molten state and completely insoluble in the solid state.

(d) They form no intermediate compounds.

The mole fraction of one component, N_A, will vary with the solution melting point temperature, T, and may be found from either of the two expressions:

$$\ln N_A = -\frac{\Delta H^*_{MA}}{R}\left[\frac{1}{T} - \frac{1}{T^*_A}\right]$$

or

$$\ln N_A = -\frac{\Delta H^*_{M}}{R}\left[\frac{1}{T} - \frac{1}{T^*_A}\right] + \frac{(C^*_A) - <C^*_A>}{R}$$

$$\left[\ln\frac{T}{T^*_A} + \left(\frac{T^*_A - T}{T}\right)\right]$$

N_A = Mole fraction of the pure substance, A.
ΔH^*_{MA} = Heat of fusion of pure substance, A, at T^*_A, cal/mole.
R = Universal gas constant, cal/mole degrees C.
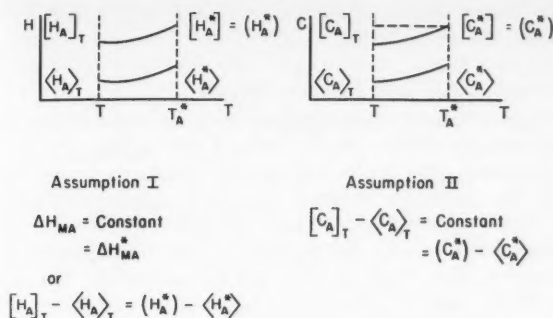T^*_A = Fusion temperature of pure substance, A, degrees K.

Assumption I

$$\Delta H_{MA} = \text{Constant}$$
$$= \Delta H^{*}_{MA}$$

or

$$[H_{A}]_{T} - \langle H_{A}\rangle_{T} = (H^{*}_{A}) - \langle H^{*}_{A}\rangle$$

Assumption II

$$[C_{A}]_{T} - \langle C_{A}\rangle_{T} = \text{Constant}$$
$$= (C^{*}_{A}) - \langle C^{*}_{A}\rangle$$

Figure 3—Assumptions I and II.

$T =$ Temperature of complete melting of solution, degrees K.

$(C^{*}_{A}) =$ Specific heat at constant pressure of molten pure substance, A, at the fusion point, cal/mole degrees C.

$\langle C^{*}_{A}\rangle =$ Specific heat at constant pressure of pure substance, A, in the solid state at T^{*}_{A}, cal/mole degrees C. This may be expressed in terms of the temperature as $\langle C_{A}\rangle = a + bT + cT^{2} + e/T^{2}$, where a, b, c, and e are constants characteristic of the substance.

$(\ ) =$ Indicates the liquid state.
$\langle\ \rangle =$ Indicates the solid state.
$[\ ] =$ Indicates dissolved substance.

The first of these expressions assumes that the heat of fusion is constant for all concentrations of "A" and is equal to the value at the melting point of the pure component as shown in Figure 3, Assumption I. The second includes a correction which takes into account the difference in specific heats between the solid and liquid phases of the pure solvent as shown in Figure 3, Assumption II.

Further refinement is possible in the form of a third assumption that the specific heat of "A" in the dissolved state is constant over the range of composition (dashed line, Figure 3) while the specific heat in the undissolved solid state may be expressed in terms of the temperature. This results in a more complicated form of expression than II but produces insignificant changes in the calculated values of N_{A}.

The first of the above expressions is intended to be used only where the solution approaches pure "A" in composition. A further extension of the range of composition is possible using the second expression, but even in this case its application to actual fuel ashes would yield approximate values at best, since such ash mixtures may not form ideal solutions.

In one case where experimental data were available, for the $Na_{2}SO_{4}$ - $MgSO_{4}$ system,[5] good agreement was found between such data and calculated values obtained by means of the second equation, as shown in Figure 4. It was assumed that no intermediate compounds form. If such compounds do exist, the experimental curve departs from calculated values as shown in the 0.45 to 0.7 range of N_{A}. Assuming that these expressions are valid, it is apparent that on a mole basis, the lowering of the fusion point of substance "A" depends on the characteristics of "A" and the quantity of added substance, "B". When the fusion point lowerings of two substances are calculated, and the curves plotted from opposite sides of the diagram, they will inter-
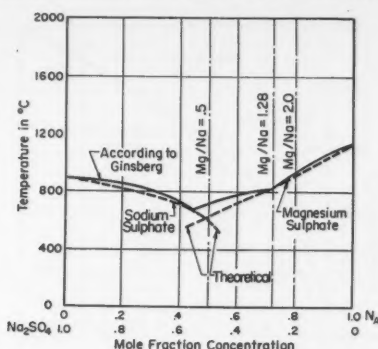

Figure 4—Experimental and calculated freezing point diagrams for magnesium sulfate with sodium sulfate.

sect at a point as shown in Figure 4. This will represent the lowest temperature at which any liquid can appear and is defined as the eutectic temperature.

In the above formulas, all values are available except the specific heat of the melted material, (C^{*}_{A}), which has seldom been determined for the high melting point compounds such as MgO. Also, the specific heat of pure solid $\langle C^{*}_{A}\rangle$ may be in error, since the range of temperatures covered by the equation do not extend to the fusion points of the compounds.

Estimate of (C^{*}_{A})

An estimate of (C^{*}_{A}) may be obtained as follows: Using the first equation, the melting point diagram may be plotted for the compound in question. From published phase diagrams,[7,8] several binaries may generally be found which contain the compound in question as one of the components. Eutectic temperatures and the corresponding concentrations from such diagrams may be plotted on the calculated diagram. In general, these points will lie below the calculated curves, indicating the necessity for the specific heat correction.

Eutectics should be chosen for relatively high concentrations to lessen the possibility of encountering an intermediate compound, and no eutectic containing such a compound should be used. Several points are desirable in order to minimize the errors prevalent in any physical test. A segment of the curve most nearly satisfying these points is then drawn from the fusion point of pure compound and a convenient value of molar concentration and corresponding temperature selected from this segment. These values may be then inserted in the second equation and a value for (C^{*}_{A}) computed. With this value for (C^{*}_{A}), the second equation may now be evaluated throughout the required temperature range.

The calculation of specific heats by such a method implies that the mixtures of inorganic salts for which freezing point data were available are ideal solutions, and it should be noted that such calculated values are only first approximations. However, the incorporation of the experimental points may partially compensate for any departure from ideal solutions and variation in solubilities. Here again the correction must be considered only approximate since these characteristics prob-
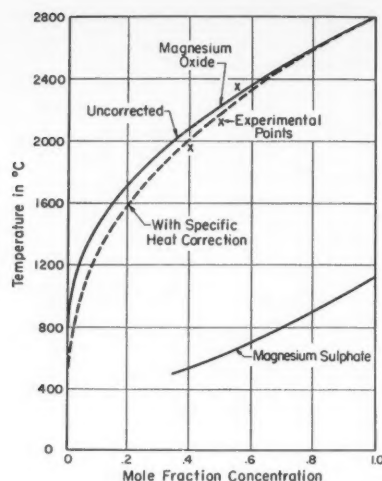
Figure 5—Calculated freezing points of magnesium compounds.

ably vary throughout the range of composition. This procedure, incidentally, might be proposed as a method of obtaining approximate specific heats at the fusion points of high melting point compounds where physical measurements would be extremely difficult. Only observed melting points of mixtures of the compounds are necessary.

Magnesium Oxide

Table 1 shows a sample calculation for magnesium oxide using the first equation. The data are plotted on Figure 5 and three experimental points are shown. From the dashed curve fitting these points, a value of $N_A = 0.5$ at 2190 C was taken, and using the second equation, $(C^*_A) = 18.86$ cal/mole degrees C was obtained. Table 2 shows a continuation of the sample calculation using the second equation with the value of (C^*_A) obtained above. These data are also plotted on Figure 5.

Magnesium Sulfate

The calculated curve for magnesium sulfate also is shown on Figure 5. Here, no correction was made for the change in specific heat, since the several test points fell exactly on this curve.

Aluminum Oxide and Silicon Oxide

Figure 6 shows data for aluminum oxide and silicon oxide. Since aluminum sulfate decomposes at a low temperature (without melting), it was not calculated. Silicon dioxide may exist in several different forms and may change slowly or quickly from one form to another as the temperature is varied. Since each form has its corresponding thermochemical constants, and, since it was not known which form or combination of forms was represented by available experimental curves, (C^*_A) was not computed. The two curves shown on Figure 6 are for quartz and cristobalite. Mixtures of the

two forms might conceivably result in a curve between the two shown.

Calcium Oxide and Calcium Sulfate

Figure 7 shows the calculated data for calcium oxide and calcium sulfate. In the case of the sulfate, the experimental data again fell on the calculated curve so that no correction resulted. Figure 8 shows calculated data for sodium sulfate and vanadium pentoxide. A value for (C^*_A) for the pentoxide of 45.6 cal per mole degree C was available,[9] but its use caused no change in the calculated curve.

Composites

Figures 9 and 10 show composites of all the oxides and sulfates examined, together with vanadium pentoxide and sodium sulfate, respectively. The intersection of each of these curves plotted from the right-hand side of the diagram with the pentoxide or sulfate plotted from the left represents the theoretical eutectic point. From such curves, it appears that variations in the amount of an additive should have little effect on the sintering or deposit forming characteristics of an ash, since this probably depends on the eutectic temperature which, in turn, is independent of the composition. At most, an additive can only raise the sinter point to a temperature which approaches the fusion temperature of the corrosive compound. This is evident from the intersections for aluminum and magnesium oxides in Figures 9 and 10. However, the quantity of eutectic material may be so small that no liquid is evident when the ash reaches the eutectic temperature. Of course, if compounds containing elements from the ash and additive are formed, these calculated curves give no indication as to the actual curves.

Although solid insolubility was assumed in the development of the freezing point expressions, a certain amount of solid solubility may be advantageous. Figure 11-a illustrates a case of solid insolubility. The solidus temperature is seen to have a constant value over the whole range of composition. Figure 11-b shows the effect of solid solubility. Here it should be possible to raise the sintering point of the ash by using sufficient additive as shown by the dashed line of composition.

Ash fusion tests have shown magnesium additives to be quite ineffective in raising the sintering temperature whereas aluminum produces noticeable increases, indicating the possible formation of solid solution. In practice[10,11] both aluminum and silicon additives have shown

TABLE 1—Evaluation of the First Equation for Magnesium Oxide

t°C	T°K	$\frac{1}{T} \times 10^3$	$\frac{1}{T^*_A} \times 10^3$	$\left(\frac{1}{T} - \frac{1}{T^*_A}\right) \times 10^3$	$\frac{\Delta H^*_{MA}}{R}$	$(\ln N_A)_1$	$\left(\frac{1}{N_A}\right)_1$	$(N_A)_1$ %
2700	2973	.3364	.3254	.0110	9311	− .1024	1.108	90.3
2500	2773	.3606	.3254	.0352	9311	− .3277	1.388	72.0
2300	2573	.3887	.3254	.0633	9311	− .5894	1.803	55.5
2100	2373	.4214	.3254	.0960	9311	− .8938	2.444	40.9
1900	2173	.4602	.3254	.1348	9311	−1.2551	3.508	28.5
1700	1973	.5068	.3254	.1814	9311	−1.6889	5.414	18.5
1500	1773	.5640	.3254	.2386	9311	−2.2215	9.221	10.8
1300	1573	.6357	.3254	.3103	9311	−2.8890	17.98	5.6
1100	1373	.7283	.3254	.4029	9311	−3.7512	42.42	2.4
900	1173	.8525	.3254	.5271	9311	−4.9076	133.5	0.7
700	973	1.0277	.3254	.7023	9311	−6.5388	960	0.1
500	773	1.2937	.3254	.9683	9311	−8.9735	8000	0.01

NOTE: $T^*_A = 3073°K$ $\Delta H^*_{MA} = 18500$ cal/mole $R = 1.987$ cal/°K
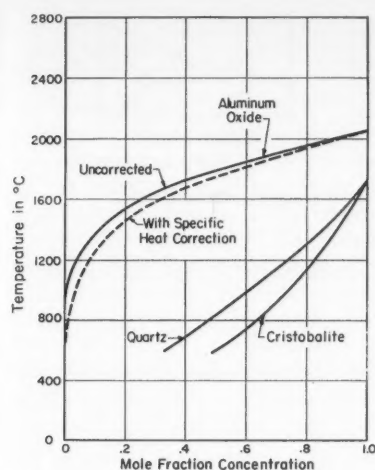
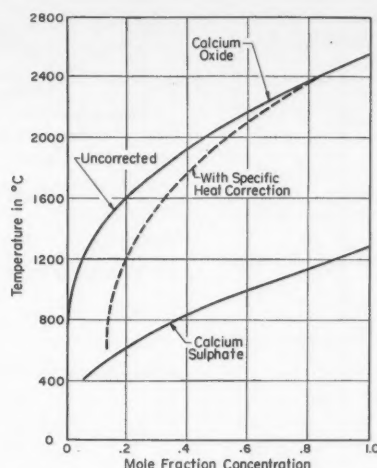Figure 6—Calculated freezing points of silicon oxide and aluminum oxide.

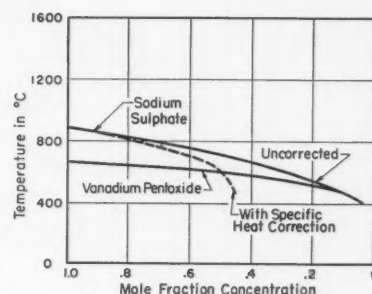Figure 7—Calculated freezing points of calcium compounds.

Figure 8—Calculated freezing points of sodium sulfate and vanadium pentoxide.

less tendency to produce deposits than magnesium. Briefly, it may be concluded, on the basis of the theoretical data, that magnesium and calcium would be excellent additives if they were present as oxides. However, as sulfates, they are undesirable. Although silicon oxide has a lower melting point than either magnesium or calcium oxide, it would appear to have an advantage in not forming a sulfate. Aluminum is, perhaps, the best compromise. While its oxide has a somewhat lower melting point than that of either magnesium or calcium, it will be shown presently that its sulfate, although stable at some conditions, reverts to the oxide at a relatively low temperature.

Thermal Dissociation of Ash Constituents

In the primary combustion zone of a gas turbine, conditions depart so far from equilibrium that thermodynamics is powerless to predict the form of fuel ash constituents and additives leaving the zone. However, in the secondary combustion region, the residence time in a given environment may be sufficiently long that a thermodynamic analysis becomes significant. On this premise a study of the dissociation of some of the metallic sulfates, previously mentioned, has been made.

If a chemical reaction takes place in a gas mixture so that substances A, B, C, . . . are transformed into L, M, N . . . according to the reaction,

$$n_a A + n_b B + n_c C + \ldots = n_l L + n_m M + \ldots$$

TABLE 2—Evaluation of the Second Equation for Magnesium Oxide

t°C	T°K	$\dfrac{(C^*_A)-\langle C^*_A\rangle}{R}$	$\dfrac{T}{T^*_A}$	$\ln\dfrac{T}{T^*_A}$	$\dfrac{T^*_A-T}{T}$	(1)	(2)	(3)	$\left(\dfrac{1}{N_A}\right)^2$	$(N_A)_2$ %
2700	2973	2.1842	.9674	—.0334	.0336	.0002	.0004	—.1020	1.107	90.3
2500	2773	2.1842	.9023	—.1026	.1082	.0056	.0122	—.3155	1.371	72.9
2300	2573	2.1842	.8373	—.1773	.1943	.0170	.0371	—.5523	1.737	57.6
2100	2373	2.1842	.7722	—.2585	.2950	.0365	.0797	—.8141	2.257	44.3
1900	2173	2.1842	.7071	—.3464	.4142	.0678	.1481	—1.1070	3.025	33.1
1700	1973	2.1842	.6420	—.4434	.5575	.1141	.2492	—1.4397	4.220	23.7
1500	1773	2.1842	.5769	—.5499	.7332	.1833	.4004	—1.8211	6.179	16.2
1300	1573	2.1842	.5119	—.6699	.9536	.2837	.6197	—2.2693	9.673	10.3
1100	1373	2.1842	.4468	—.8056	1.2382	.4326	.9449	—2.8063	16.56	6.0
900	1173	2.1842	.3817	—.9632	1.6198	.6566	1.4341	—3.4735	32.25	3.1
700	973	2.1842	.3166	—1.1503	2.1583	1.0080	2.2017	—4.3371	76.49	1.3
500	773	2.1842	.2515	—1.3803	2.9754	1.5951	3.4840	—5.4895	242.15	.4

$$(1) = \ln\left[\frac{T}{T^*_A} + \frac{T^*_A-T}{T}\right] \qquad (2) = \text{Specific Heat Correction} \qquad (3) = (\ln N_A)_1 + (2)$$

$$(1) = \frac{(C^*_A) - \langle C^*_A\rangle}{R}$$

NOTE: $(C^*_A) = 18.86$ cal/mole °K

$$\langle C^*_A\rangle = 10.86 + 11.97 \times 10^{-4}\, T^*_A - \frac{2.087 \times 10^5}{(T^*_A)^2} = 14.52 \text{ cal/mole °K}$$

the expression for the equilibrium constant may be written

$$K = \left(\frac{N_l^{n_1} \cdot N_m^{n_m} \cdot N_n^{n_n} \ldots}{N_a^{n_a} \cdot N_b^{n_b} \cdot N_c^{n_c} \ldots}\right) P^{n_1 + n_m + \ldots - n_a - n_b - \ldots}$$

where N_i is the mole fraction of constituent "i" and P is the total pressure of the system. When some of the reactants or products are liquids or solids, the corresponding partial pressures become vapor pressures. Since these will be functions of temperature alone and will not change as the reaction progresses, they may be transferred to the left-hand side of the equation and combined with K, which is also a function of temperature alone, to form a modified equilibrium constant K′. The corresponding exponents of P are also omitted.

Dissociation of Magnesium Sulfate
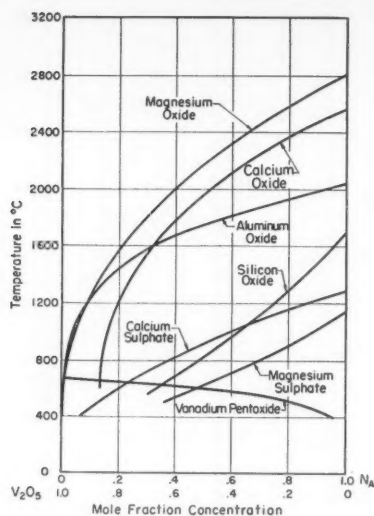
An example of the use of the equation is shown for

Figure 9—Calculated freezing point diagrams with vanadium pentoxide.
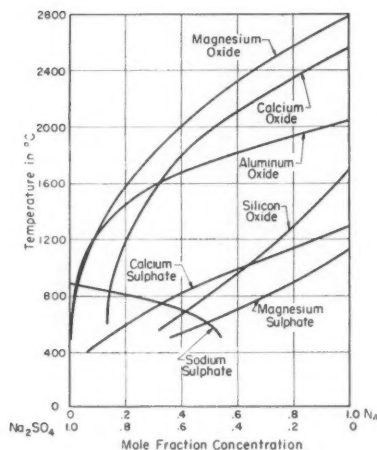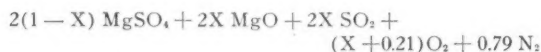

Figure 10—Calculated freezing point diagrams with sodium sulfate.

the dissociation of magnesium sulfate according to the reaction equation:

$$2\,MgSO_4 = 2\,MgO + 2\,SO_2 + O_2$$

If X is taken as the fractional molal decomposition of $MgSO_4$, the composition at equilibrium becomes:

$$2(1-X)\,MgSO_4 + 2X\,MgO + 2X\,SO_2 + (X+0.21)O_2 + 0.79\,N_2$$

where one mole of air has been included since the reaction is assumed to be taking place in an air atmosphere. This is not intended to represent the condition in an actual combuster where the air-fuel ratio might be 75 to 1, the magnesium sulfate would represent a very small part of the fuel, and the situation would be further complicated by the presence of vaporized fuel, directly formed SO_2, and other products of combustion. However, it does form a common basis for comparison of the various sulfates in question.
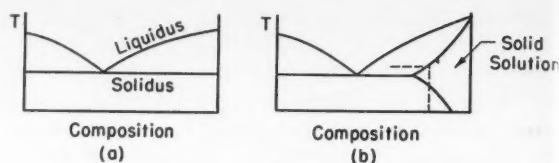
Figure 11—Solid solubility and insolubility.

The total number of moles of gaseous constituent is:

$$2X + (X + 0.21) + 0.79 = 3X + 1.0$$

and the mole fractions of the two gaseous products are:

$$N_{so_2} = \frac{2X}{3X+1}$$

$$N_{o_2} = \frac{X+.21}{3X+1}$$

Substituting in the equilibrium equation, at atmospheric pressure.

$$K' = (N_{so_2})^2\,(N_{o_2})\,P^3 = \left(\frac{2X}{3X+1}\right)^2\ \left(\frac{X+.21}{3X+1}\right)$$

Kelley[12] has tabulated values of K' for various temperatures. Taking the value at 1403 K of 4.68×10^{-2}, the equation becomes:

$$X^3 - 0.1548\,X^2 - 0.1539\,X - 0.0171 = 0$$

from which

$$X = 0.5165$$

If the same computation is made assuming a total pressure of five atmospheres, a figure more in line with gas turbine practice,

$$K' = \left(\frac{2X}{3X+1}\right)^2\ \left(\frac{X+.21}{3X+1}\right)(5^3)$$

and again for $K' = 4.68 \times 10^{-2}$

the equation becomes:

$$X^3 + 0.2080\,X^2 - 0.00084\,X - 0.000094 = 0$$

from which

$$X = 0.0221$$

In other words, at a temperature of 1403 K and atmospheric pressure, more than half the magnesium sulfate decomposes into the more desirable oxide. However, when the pressure is raised to five atmospheres, only two percent decomposes. This may explain why Sulzer[10] found magnesium to be an excellent additive at atmospheric pressure but ineffective, and in fact deposit forming, at 25 atmospheres. Furthermore, it indicates that caution should be used in predicting the behavior of an additive in a turbine operating at high pressure from results obtained in atmospheric test rigs. The temperature 1403 K or 2066 F is admittedly much higher than found at the turbine inlet but might be a reasonable value for the combustor reaction zone. The calculation assumes time for equilibrium to be reached, which actually may not be the case, but if quasi-equilibrium is reached at this temperature before diluent air is admitted, it is conceivable that the reaction could be frozen, thus preventing the reformation of the constitu-

ents which would normally exist at the lower temperature condition.

Other Sulfates

Similar calculations for the calcium, aluminum and sodium systems showed calcium and sodium sulfates to be the stable forms at this temperature, but the aluminum sulfate would be almost completely decomposed to oxide at a temperature of 800 C at atmospheric pressure and 920 C at five atmospheres. Figure 12 shows these dissociation results graphically.

Figure 12—The effect of pressure and temperature on the dissociation of various sulfates to oxides.

Summary

While the results of the calculations presented herein must be considered speculative due to the simplifying assumptions regarding the character of the chemical mixtures, they nevertheless lead to some interesting conclusions and indicate a fertile field for further investigation of the possibility of reducing fuel ash corrosion by the use of inhibiting additives.

On the basis of the calculated melting point curves, the following conclusions may be reached.

1. Refractory metallic oxides such as those of aluminum, calcium, magnesium, and silicon appear to be more effective than other compounds (viz., sulfates of these elements.)

2. Magnesium oxide having the highest melting point and a high heat of fusion should be the most effective in raising fuel-ash melting points although the higher heat of fusion of aluminum oxide enhances its effectiveness.

3. Binary mixtures which satisfy the simplifying assumptions should have sintering points corresponding to the eutectic temperature and this temperature will be below the melting point of the pure corrosive compound. In the event that some solid solubility occurs, it may be possible for an additive to raise the sintering point.

The dissociation calculations lead to some modifications of these conclusions. Since all residual fuels contain considerable sulfur (one to three percent by weight), some sulfate will be almost certain to form in the primary combustion zone. Such sulfate may decompose in the secondary zone if temperature and residence time permit such a transformation to occur. The conclusions are then supplemented as follows:

1. Aluminum compounds should be the most satisfactory of the metallic additives investigated, since aluminum sulfate dissociates to form the oxide at temperatures only slightly above prevailing turbine inlet temperatures.

2. Magnesium compounds should be less satisfactory, since the sulfate dissociation occurs at temperatures well above prevailing turbine inlet temperatures.

3. Calcium compounds should be the least desirable, since the sulfate dissociation starts far above prevailing turbine inlet temperatures.

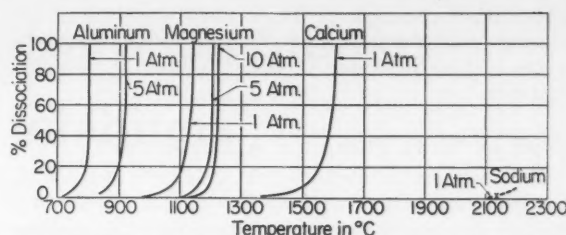4. Since the sulfate dissociation reactions are pressure dependent, the behavior of all proposed residual fuel additives should be investigated at turbine operating pressures.

Although more extensive and accurate thermochemical data would contribute to the validity of the results of such studies of ideal binary mixtures, the results already obtained have been useful in indicating promising avenues of investigation of additives to prevent fuel-ash corrosion. However, all conclusions must be carefully verified by tests which reproduce actual operating conditions as closely as possible.

The experimental investigation of ash fusion behavior is being continued with the aid of a Leitz Heating Microscope in order to extend the temperature range up to 1600 C. X-ray diffraction studies of ash-additive mixtures to detect the presence of mixed crystals and compounds are also in progress.

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DISCUSSION

Question by David W. McDowell, The International Nickel Company, Inc., New York, New York:

If the precious metals resist the attack of residual fuel oils, would it be feasible to plate materials to

afford this protection? It is understood that this plating would be performed on the first two stages of a gas turbine designed to burn Bunker "C" residual fuel oils.

Reply by W. E. Young and A. E. Hershey:

Precious metal coatings are a definite possibility. Fuel contaminants in their liquid state apparently remove protective oxide films from refractory alloys. If no oxide film is present this type of attack should not take place. Attempts at cladding with platinum and dipping in a platinum-gold alloy have not been too successful to date, but platinum plating has shown some promise. Unfortunately, the quality of coating is not consistent and whereas some specimens have shown some degree of resistance, others contain surface imperfections which permit attack to start on the base metal. Once such attack starts, the liquid ash works under the coating and peels off sections of the material. Finally, although such coatings are admittedly expensive, an economic study indicated that a reasonable blade life coupled with the decreased cost of fuel preparation would make their use feasible.

Question by H. Howard Bennett, Socony Mobil Oil Co., Inc., Paulsboro, New Jersey:

Have you determined the optimum or desirable particle size of additives when added as slurries?

Reply by W. E. Young and A. E. Hershey:

We have made no full scale passage tests with slurries containing sized particles. However, ash fusion tests were made with three sizes of aluminum oxide as an additive. A coarse powder, in the range of 325 mesh, had no apparent effect on the ash

melting point. Powder in the range of 1 to 5 microns increased the melting point but not to the extent of a submicron suspension in oil. On the basis of such tests we feel that as fine a suspension as possible intimately mixed, should be used. Ultimately, an oil soluble additive would be desirable.

Questions by David Roller, Dayton, Ohio:

Dr. Young in his paper mentioned the fact that a large number of tests were made in crucibles while determining the effect of fuel oil ash corrosion on several alloys and coatings. Were any alloy or coating constituents preferentially leached by the corrodent? Was there any consistency to the attack? What methods were used to determine if such an attack occurred?

Replies by W. E. Young and A. E. Hershey:

Preferential attack was most noticeable in the case of Stellite where this attack seemed to be concentrated at the grain boundaries. Scale and deposit resulting from passage tests were frequently quite blue and X-ray diffraction tests confirmed the presence of large amounts of cobalt. The attack in the case of Inconel X and 25/20 stainless on the other hand did not seem to be preferential in this sense. For example, the stainless exhibited large pits which must have contained all three of its basic constituents. The most general attack occurred with a cemented carbide which corroded quite smoothly and uniformly over its entire surface. Metallographic analysis of the specimens was used to determine the nature of the attack and this information was frequently supplemented by spectrographic, X-ray diffraction, and wet chemical analysis of the deposit and scale in the attacked region.

Any discussions of this article not published above
will appear in the December, 1957 issue.

Corrosion and Adsorption Studies Using Sulfonate Inhibitors*

By A. H. ROEBUCK,* P. L. GANT,* O. L. RIGGS* and J. D. SUDBURY*

Introduction

THE VALUE of sulfonates as corrosion inhibitors has been demonstrated repeatedly by laboratory experiments and field usage. Probably more sulfonates have been used than any other class of corrosion inhibitors. They are used as rust preventatives in lubricating oils, slushing oils, gasolines, internal cooling systems, product pipe lines, and storage of steel parts.

Much effort has been expended to establish useful formulations of sulfonates. Very little work has been done, however, to establish the mechanism of corrosion inhibition due to sulfonates. Considerable work has been done to show that other polar organic molecules (such as acids and amines) inhibit by means of adsorption at anodic[1] or cathodic areas[2,3,4] of steel surface. Most of the recent papers[5,6,7,8,9,10,11] have concluded that adsorption occurs at both anode and cathode areas. It has been shown further that the effectiveness of such inhibitors is due not so much to the total adsorbed film but to the chemisorbed film which cannot be readily removed by desorption techniques.

One recent paper[12] has proposed that the strength of the adsorption bond (and thus the effectiveness as an inhibitor) can be predicted on the basis of the electronic structure of the adsorbed group. Those groupings with high electron density are shown to be the most effective. This theory fits well the relative behavior of various amines, acids, mercaptans, alcohols, phenols, esters, aldehydes, and ketones as corrosion inhibitors; however this theory predicts that sulfonates should not have inhibitive properties. It was postulated by Hackerman that the known effectiveness of sulfonates as inhibitors might be due to the presence of impurities.

Radiometric adsorption studies[13] of a calcium sulfonate from oil showed the extent of adsorption to be increased greatly by the addition of small amounts of water. Based on these data, Van Hong and associates concluded that calcium sulfonate adsorption was effected by means of chemisorption rather than physical adsorption.

Powers and Cessna[14] propose the polar-type oil inhibitors function by promoting the passivation of iron and steel by concentrating the dissolved oxygen

Abstract

The existing literature pertaining to the use of sulfonates as corrosion inhibitors is reviewed briefly. An account is given of radiometric adsorption and desorption studies made of sodium and amine salts of sulfonic acids. Corrosion inhibitor studies also were made of these salts in H_2S and CO_2 environments; some of the variables encountered include the effect of: (1) concentration, (2) solubility, (3) molecular weight, and (4) extent of neutralization of sulfonic acid. A simplified explanation of the mechanism of sulfonate inhibitors also is given. **5.8.3**

at the metal-oil interface—thus providing an environment favorable for oxidation.

A sequestration of the corrosive acid by micelles in the oil is a mechanism of inhibition with sulfonates presented by Baker, Singleterry and Solomon.[15]

To date, there is no published work adequately describing a mechanism of corrosion inhibition due to sulfonates.

The remainder of this paper has been written to describe:

1. Radiometric adsorption and desorption studies of sodium and amine salts of sulfonic acids.

2. Corrosion inhibitor studies of these same salts in H_2S and CO_2 environments. Some of the variables considered in these studies include the effect of (a) concentration, (b) solubility, (c) molecular weight, and (d) extent of neutralization of sulfonic acid.

3. A simplified explanation of the mechanism of sulfonate inhibitors.

Experimental Procedures

Inhibitor Preparation

The inhibitors used in the corrosion experiments were prepared according to the following procedures. The procedures are not specific for sulfonation of each oil fraction of dodecylbenzene. The amount of ingredients and temperatures vary according to the molecular weight of fraction used.

Preparation of Sulfonic Acid. A selected oil (fraction of dodecylbenzene), the amount depending on the molecular weight of the oil fraction, was weighed into the flask. The hydrocarbon was cooled to 10 C. Oleum 20 percent was added very slowly over a period of 30 minutes with slow stirring to prevent

Figure 1—Proposed inhibitor structures.
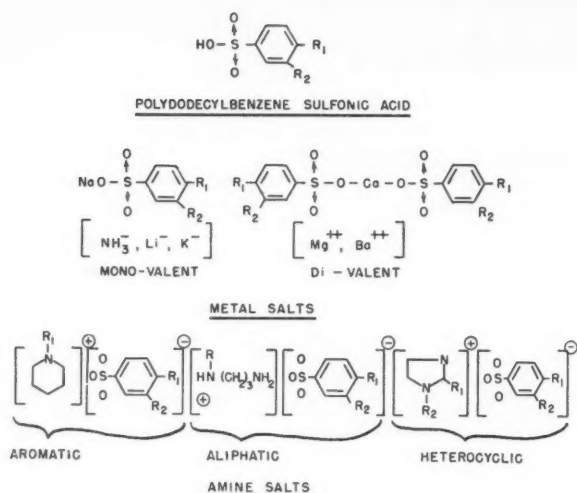

Figure 2—Corrosion apparatus.

splashing. The mole ratio of oleum to hydrocarbons was 8:1. The temperature was kept below 30 C during the reaction. After all the acid had been added, the temperature was raised to 37 C and the contents were stirred for one hour. Contents were cooled to 25 C, stirring was stopped, and a small amount of ice was added. The temperature was raised to approximately 70 C, then cooled to 65 C, and stirred vigorously for five minutes. The contents of the flask were poured into a separatory funnel, and the mixture was allowed to separate. The bottom portion was drawn off and discarded. The sulfonic acids made by this procedure are about 65 percent active sulfonic acid and 35 percent unreacted hydrocarbon.

The structure of a typical polydodecylbenzene sulfonic acid is shown in Figure 1. The actual product is a mixture of sulfonic acids with one or more highly branched substituted R groups.

Metal Neutralization of Sulfonic Acid. The desired amount of sulfonic acid was weighed into a separatory funnel and diluted with benzene. The metal hydroxide was prepared as a water solution. For example a 25 percent NaOH solution was used for corresponding sulfonate. The metal hydroxide solution was stirred continuously while the sulfonic acid was added. The addition of sulfonic acid was made rapidly enough to maintain a temperature of 50 C or below. When the reaction was completed, the product had a pH of 7-8. The undesired salts were filtrated from the final product. The structures of mono- and di-valent metal sulfonates are given in Figure 1.

Amine Neutralization of Sulfonic Acid. The desired amount of amine was weighed into a standard organic reflux setup. The temperature of the amine was raised to approximately 75 C. The contents were stirred moderately as the predetermined
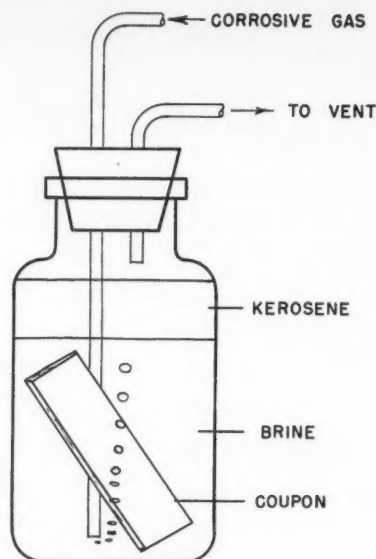
amount of sulfonic acid was added. The addition of sulfonic acid was made slowly over a period of 30 to 40 minutes. The temperature of blend was raised to 85 C, and stirred vigorously for five minutes. No filtration was needed. Structures of the aromatic, aliphatic, and heterocyclic amine sulfonates appear in Figure 1.

Corrosion Tests

In order to determine the inhibitive properties of sulfonates, several types of laboratory corrosion tests were performed. These included tests in (1) H_2S—kerosene-brine system, (2) CO_2—kerosene-brine system, and (3) H_2S—CO_2—kerosene-brine system. Figure 2 shows a "bubble test" cell as used in making these tests. The brine used was 5 percent NaCl.

The designated corrosive gas was supplied to the systems at a desired rate. The inhibitor under investigation was studied over a concentration range of from 5 to 500 ppm dissolved in the liquid phase.

The system under study were agitated either by mechanical action or by the bubble action of the gas addition. Except for the CO_2—kerosene-brine system, the temperature of the tests was controlled at 75 F (24 C) in a thermostated room. The CO_2 test equipment was run in a constant temperature water bath at 120 F (48 C).

Coupons cut from 1020 plain carbon, cold rolled steel sheet were used as test specimens. Surfaces were prepared by abrasion on 80 grit Aloxite paper. Inhibitor evaluations were based on sample appearance and weight change.

The effectiveness of an inhibitor was based on the formula:

$$\text{Percent Effectiveness} = \frac{W_1 - W_2}{W_1} \times 100$$

W_1 = Weight Loss of Blank Coupon
W_2 = Weight Loss of Inhibited Coupon

Adsorption Studies

Several adsorption experiments were carried out using radio-tagged polydodecylbenzene sulfonates as sorbates. Polydodecylbenzene having an average molecular weight of 370 was sulfonated by the addition of oleum. A yield of approximately 70 percent total was obtained. Sulfur -35 was used as a radiotracer element. Approximately 30 millicuries of active sulfur were used. The activity of the tagged sulfonic acid as prepared was 10^7 disintegrations per second per gm. The acid was reacted with the appropriate base to form the desired sulfonate. Measurements were made on one-inch diameter, round, flat 1020 steel coupons. The coupons were approximately 3/16 of an inch in thickness and were polished using a belt grinder with 120 Aloxite grit. In order that the coupons be ground flat, a special chuck was made to hold them while polishing. The coupons were washed with isopropyl alcohol, acetone, and iso-octane after polishing. They were dried and stored in a vacuum desiccator.

The adsorption process was carried out by placing the coupons in a solution of the desired concentration of sulfonate in dry iso-octane at 24 C. Fifty milliliters of solution were used. The coupon was immersed in this solution and allowed to stand without agitation for the desired period of time. The coupon was then removed and rinsed in four successive rinses of dry iso-octane without allowing the surface to become dry between rinses. Following rinsing, the coupon was dried under an infrared lamp. The counting rate was not affected by the drying procedure.

The coupons were counted in a flow counter. They were placed in a stainless steel cup which absorbed all sulfur-35 radiation from the sides and bottom of each coupon. A measured volume of the 100 ppm solution was counted under similar geometric conditions (on the same type of coupon) to give the ratio of the counts per minute per mircogram. In this manner the absolute weights of the adsorbed inhibitor were determined to within 1/10 of a microgram through the use of radio-tracer techniques.

A check adsorption experiment was carried out using 1020 steel powder having a known surface area. The adsorption taking place was determined by the change in solution concentration as measured by radio-tracer techniques.

The coupons were desorbed by placing them in clean iso-octane at 24 F and allowing them to soak for measured periods of time.

The effectiveness of the adsorbed inhibitor in preventing corrosion was determined by exposing the coupon to an H_2S-brine system and measuring the time required for the corrosion reaction to proceed until a uniform black iron sulfide corrosion product is formed. This test is referred to as the "time to to blackening test."

Experimental Results

Laboratory Corrosion Tests

Metal Salts of Sulfonic Acid as Inhibitor. Metal salts of dodecylbenzene sulfonic acid and polydode-
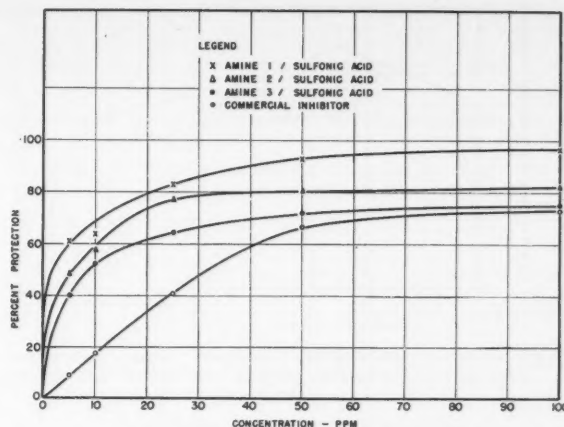
Figure 3—Corrosion rate of steel in 3 parts water, 1 part kerosene and 0.8 L/M hydrogen sulfide.

cylbenzene sulfonic acid were tested as inhibitors. The molecular weight of dodecylbenzene sulfonic acid ($C_{12}H_{25} - C_6H_4 - SO_3H$) is 326. Metal salts of this acid, such as sodium dodecylbenzene sulfonate, were not effective as corrision inhibitors under the conditions of test. This acid and its monovalent metal salts were only slightly oil soluble.

Increasing the molecular weight of the hydrocarbon portion of this compound increased its oil solubility. Increased oil solubility resulted in increased inhibitor effectiveness up to a certain point. For example, the sodium salt of polydodecylbenzene sulfonate ($(C_{12}H_{25})_x - C_6H_4 - SO_3Na$), having an average molecular weight of about 470 ± 20, had much greater H_2S inhibitive properties. At a concentration of 95 ppm (0.002 mole per liter), it showed an effectiveness of about 80 percent. Other monovalent salts of polydodecylbenzene sulfonic acid tested were lithium and potassium. Both showed an effectiveness of about 80 percent at 95 ppm.

The use of dibasic salts, such as calcium, resulted in sulfonates with increased oil solubility. This salt had an average molecular weight of 940 ± 30. In concentrations of 0.00001 molar, it showed excellent inhibitive effects against CO_2-kerosine-brine system at 48 C. Corrosion rates of a blank in this system were 120 mpy initially and 15 mpy after two days of free corrosion. The addition of 10 ppm calcium sulfonate reduced the initial rate of corrosion to 6 mpy. After two days, the rate of attack was 0.7 mpy. Sodium and ammonium polydodecylbenzene sulfonates were less effective in the CO_2 system.

Amine Salts of Sulfonic Acid as Inhibitor. Several amine polydodecylbenzene sulfonate salts were prepared and tested. Many showed outstanding inhibitive properties. Figure 3 shows the percent protection afforded by such compounds at several concentrations as compared with a commercially used oil well corrosion inhibitor (imidazoline type). The outstanding feature afforded by amine sulfonates was the high degree of protection afforded at low concentrations. This provided a safer and more effective
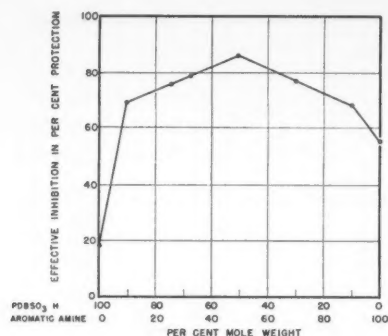
Figure 4—Improved inhibition due to aromatic amine-sulfonic acid reaction products.
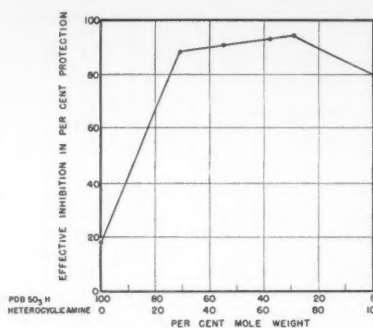
Figure 5—Improved inhibition due to heterocyclic amine-sulfonic acid reaction products.
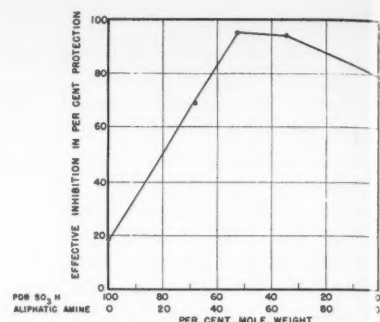
Figure 6—Improved inhibition due to aliphatic amine-sulfonic acid reaction products.

inhibition for oil wells in which the inhibitor was added batchwise.

Various mole percents of polydodecylbenzene (PDB) sulfonic acid were reacted with selected amines. These amine types included (1) aromatic, (2) heterocyclic, and (3) aliphatic. The molecular weight range of the amines was from 170-400. The effective inhibition of each amine PDB sulfonate reaction mixture was tested at a concentration of 25 ppm. In each case the effectiveness of the amine was increased by the addition of PDB sulfonic acid. The use of amines that were shown not to be corrosion inhibitors when reacted with PDB sulfonic acid, produced effective inhibitors. Improved inhibition characteristics also were attained by adding the PDB sulfonic acid to amines that were known to be effective corrosion inhibitors. Improvements were particularly noticed at very low concentrations.

Figure 4 illustrates the effect of varied mole weight ratios using aromatic amine compounds with PDB sulfonic acid. Maximum effectiveness is attained by using reaction mixture of amine and acid in a 49/51 mole ratio. The effectiveness of the reaction mixture is decreased as this mole ratio is either increased or decreased. Maximum effectiveness of this inhibitor is reached over a very narrow range of ratios, but appreciable effectiveness is achieved over a wide range of ratios.

Figure 5 shows a wide mole weight range in which nearly maximum effective blends can be made using heterocyclic amines with the PDB sulfonic acid. The effective mole weight range is wide enough that the amine/acid ratio can be off considerably without reducing the effectiveness of the final blend significantly. As much as 70 percent mole weight of PDB sulfonic acid can be used without losing much effectiveness. This fact makes formulation problems much easier and more economical, since these sulfonic acids are cheaper than the heterocyclic amines.

In Figure 6 the same type of data are shown for an aliphatic amine salt. The mole weight range over which maximum effectiveness is obtained is very narrow. The effectiveness decreases sharply to the acid end from the point of maximum effectiveness. A very effective corrosion inhibitor could be made within mole ratio limits of 51/49 to 35/65.

Other desirable properties made possible by the addition of PDB sulfonic acid to the amines are not revealed by the graphs.

Included in these properties are such things as:

1. Improved oil solubility of the amine for blending purposes.
2. Improved water dispersibility for more effective inhibition.

Oil solubility of corrosion inhibitors for use in the producing oil well is desired. Some of the low molecular weight amines are not soluble in oils. This oil insolubility property is partially changed by reaction with PDB sulfonic acid. To make the oil soluble corrosion inhibitor even more effective, it should be partially water dispersible. The high molecular weight amines are formulated to have this property by reaction with PDB sulfonic acid.

Adsorption Experiments

In order to gain a better understanding of the mechanism by which sulfonates provide inhibition, several adsorption tests were run in conjunction with corrosion tests. The corrosion tests were performed on the coupons used in the adsorption tests in order to correlate inhibition with adsorption.

Figure 7 shows typical adsorption isotherms for sodium sulfonate and an amine sulfonate. The breakover point of the curve was about 3.3 micro moles per cm.^{2} x 10.^{4} Assuming a molecular area of about 50 sq Å and a surface roughness factor of 2, approximately one half of the surface is covered by a monomolecular layer at 10 ppm. Assuming the same molecular area and roughness factor, the surface coverage at 100 ppm was 0.84 and 0.64 monolayers respectively for the amine sulfonate and sodium sulfonate.

In order to check these adsorption measurements, duplicate experiments were carried out using steel powder having a known surface area instead of the steel coupons. The steel powder was allowed to come to adsorption equilibrium, and the change in solution concentration was measured to determine the extent of adsorption. The amount of adsorption taking place on the coupons, as measured by tracer counting techniques after a quick rinse, was deter-
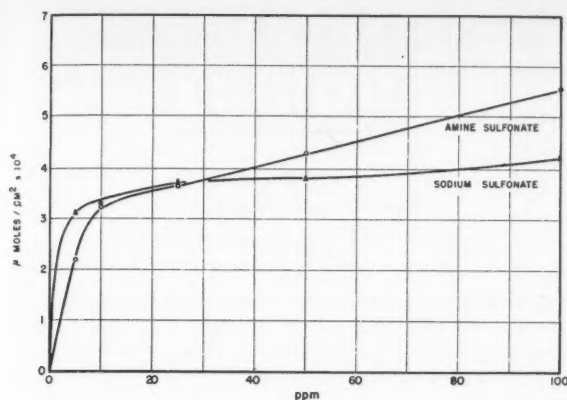
Figure 7—Adsorption of sulfonates.
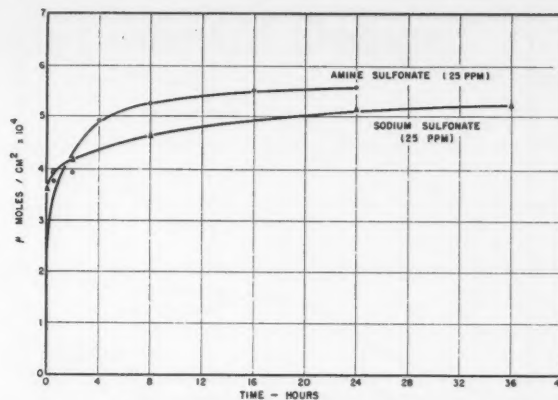
Figure 8—Rate of adsorption of sulfonates.

Figure 9—Rate of desorption of sulfonates.

mined to be 80 percent of that taking place on the steel powder.

It was necessary to rinse the steel coupons after removing them from the adsorption system in order to remove the sorbate solution remaining on their surface. This was accomplished by a quick rinse in iso-octane as previously described.

Figure 8 shows the rate of adsorption isotherms for amine sulfonate and sodium sulfonate. These isotherms were determined at 25 ppm. Although the total adsorption of sodium sulfonate did not reach as high a figure as that of amine sulfonate, it was adsorbed at a much more rapid rate.

Figure 9 shows the rate of desorption isotherms of sodium and amine sulfonates. Both isotherms were determined at 25 ppm. The sodium sulfonate was more firmly held than the amine sulfonate and showed only a slight desorption.

Figure 10 shows inhibitor effectiveness curves for specimens used in adsorption tests at various concentrations. The concentration of the sorbate in which the coupons were immersed is plotted versus time to achieve a given extent of corrosion. These curves are similar in relative shape to adsorption curves for the two inhibitors. They are also similar to the corrosion rate curves of coupons exposed in systems containing various concentrations of inhibitors. A definite qualitative relationship is seen to exist between the extent of adsorption and inhibition. These tests, unfortunately, did not predict the great superiority of the amine sulfonates over the metal sulfonates as shown in Figure 9 and in all other corrosion data obtained.

Proposed Mechanism of Inhibition by Sulfonates

Various laboratory techniques were used to show the surface-active characteristics of sulfonates. These techniques have included interfacial measurements, drop-sized ratio measurements, and adsorption measurements. All indicated that sulfonates have strong surface active characteristics.

The sulfonates as manufactured contain about 50 percent oil. Several experiments were carried out at an earlier date which indicated that the presence of oil in sulfonate inhibitors played an important role
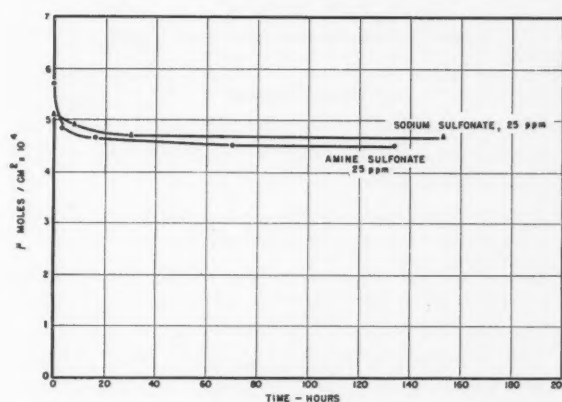
in their effectiveness. In the presence of a large excess of oil, good inhibitive properties were observed. In the presence of only a small amount of oil, inhibitive properties were poor.

In order to check this effect, a sample of sodium polydodecylbenzene sulfonate was de-oiled using a water-isopropyl alcohol-pentane extraction system. The sulfonate was extracted into the water-alcohol phase. Negligible amounts of sulfonate were left in the hydrocarbon phase as measured by radio-tracer technique. This phase was removed using a separatory funnel and was concentrated on a low-temperature hot plate.

The inhibitive effectiveness of the de-oiled fraction as determined by a corrosion test was nil. In fact, the de-oiled fraction caused a slight acceleration in the corrosion rate. Pale oil (170 V.I.) was added to the de-oiled fraction. A corrosion test on the resultant solution indicated good inhibitor effectiveness. The presence of oil apparently is required in sulfonate inhibited systems for effective inhibition. The mechanism of sulfonate inhibition must involve the "oil effect." A drawing which represents the postulated theory that the sulfonates occlude or draw oil to the metal surface as they are adsorbed is given in Figure 11. This renders the surface preferentially oil wet. The barrier layer of oil, held in place by the adsorbed sulfonate, minimizes corrosion.
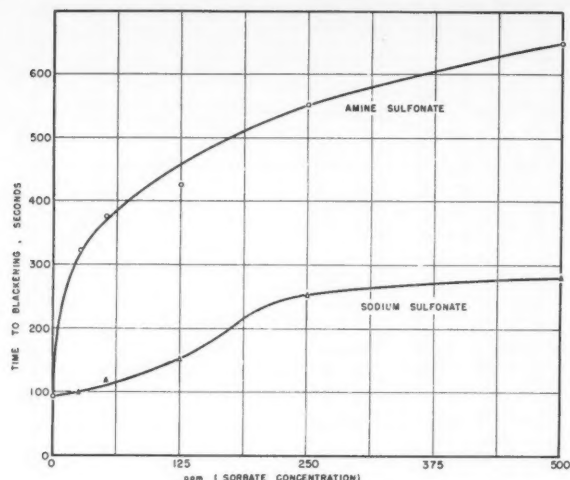
Figure 10—Corrosion of inhibited steel coupons.

Figure 11—Mechanism of sulfonate inhibition.

7. Sulfonate inhibitors are postulated to function by adsorption on the metal surface and thus make this surface preferentially oil wet. The presence of oil was shown to be essential for effective inhibition.

Conclusions

1. Effective sulfonate corrosion inhibitors were those made from sulfonic acids in the molecular weight range of 300-470.

2. Effective inhibition with certain amine sulfonates was given at concentrations as low as 5 ppm.

3. The solubility in oil or dispersibility in water can be controlled by selection of proper molecular weight sulfonic acid and amine.

4. The reaction products of amine and PDB sulfonic acid were much more effective as inhibitors than either amine or acid alone. The most effective mole weight ratio was determined by corrosion tests.

5. A radiometric technique was successful in studying adsorption-desorption characteristics of sulfonates.

6. Sulfonate inhibitors were shown to be strongly adsorbed on steel surfaces. Most of this adsorbed layer could not be readily removed by desorption.

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Some Concepts of Experimental Design*

By J. D. HROMI

Introduction

INDUSTRIAL EXPERIMENTATION, be it in the plant or in the laboratory, concerns itself with the interpretation of data in the search for answers to specific problems. When there is access to large amounts of data previously accumulated, it is natural to expect that a great deal of information pertinent to current problems can be obtained. Oftentimes, however, the information obtained from these data are not what had been expected.

Large masses of data are not likely to be useful unless they can be reduced to a form from which one can readily estimate the effect of existing conditions on the process or the product. The techniques of multiple-regression analysis and statistical quality control have enabled the plant worker and the experimenter to realize some degree of success in drawing conclusions from uncertain data. Yet, these techniques leave much to be desired. For example, the calculations required in a multiple-regression analysis are complicated and expensive, and their yield is low.

More-efficient methods of investigation have become available to the experimenter through efforts of the mathematical statistician. These relatively new methods make it possible to attain the objectives of an investigation economically and efficiently. Experimental data are collected according to some planned scheme designed to provide sound answers to specific questions. If the experiment is properly designed, the analysis of the related data should yield inferences with established confidence.

The problem of making a quantitative evaluation of the effects of several process variables or factors, such as temperature, pressure, and acid concentration, on the purity of a resulting product is typical of the problems for which a controlled comparative experiment can be planned. An experiment in which the investigator fixes the levels (given values or conditions) of the independent variables is almost always of the comparative type.

In conducting a comparative-type experiment, there is a choice of varying one factor at a time or of varying more than one factor at a time. The "classical experimenter" would make the first choice; the experimenter with the more modern approach would make the second choice. The classical concept of experimentation does not permit the use of all the responses or values of the dependent variable in making each conclusion. Nor does this concept afford the opportunity to see whether the effect or change in response due to one factor is the same for all levels of another factor. The modern concept of

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JOHN D. HROMI is head of the Statistics Section of the United States Steel Corporation's Applied Research Laboratory, Monroeville, Pennsylvania. He received a BS in mathematics from Carnegie Institute of Technology in 1948 and then was granted a BS in electrical engineering from Clemson College in 1950 and a M. Litt from the University of Pittsburgh in 1951. Mr. Hromi is a member of the American Statistical Association, the Institute of Mathematical Statistics and the American Society for Quality Control.

Abstract
Large masses of data in industrial experimentation are meaningless unless they can be reduced to a form from which it is possible to readily estimate the effect of existing conditions on the process or product. In the past, multiple-regression analysis and statistical quality control have been used in this connection with limited success. It is now possible to obtain more complete results through the use of a method developed by mathematical statisticians. This method is outlined and discussed in detail. It is shown how use of this technique enables an investigator to use each piece of data for making each conclusion and enables him to examine the behavior of one variable at more than one level of each of the other variables in the study. 2.1.1

experimentation has none of these disadvantages; hence, the factorial experiment as developed by R. A. Fisher[1] about 30 years ago is more efficient. Since all the observations are used in drawing each conclusion, each inference can be made with increased precision. The factorial experiment also enables the investigator to evaluate interaction effects if they exist. Interaction effects appear when the behavior of the responses for one factor is not the same at all levels of another factor. Only those designs which afford the aforementioned advantages will be discussed in this paper.

Planning the Design of an Experiment

It would be well at this point to review the nomenclature and symbolism that will be used in developing the experimental designs to be discussed here. To keep the illustrations general, reference shall be made to the various factors as factor A, factor B, and so on. The capital letter will also be used to represent an estimate of the effect of the corresponding factor on the measured variable. When only two levels of each factor are being studied, each run can be de-

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noted by a combination of the factors for a given level of each factor. For instance, in a two-factor experiment, the run in which factor A is at the high level and factor B is at the low level can be denoted by a small "a"; thus the presence of a letter in the combination denotes the high level of the factor and the absence of a letter from the combination denotes the low level of that factor. When both factors are at the low level, that particular run is symbolized by (1). Every run in the two-factor experiment is listed in Table 1.

A combination of factors is often referred to as a "treatment combination." When some factors are being studied at more than two levels, then 0, 1, 2, and so on can be used to symbolize the levels of the factors arranged in alphabetical order. As an example, 102 is the symbol for a treatment combination in a three-factor experiment where 1 is the second of two or more levels of factor A; 0 is the lowest level of factor B; and 2 is the third of three or more levels of factor C. Every run of an experiment in which factor A has two levels, factor B has three levels, and factor C has three levels is shown in Table 2.

To provide sound answers to specific questions, the experiment should be planned in detail. Complete familiarity with the technical aspects of the problem is obviously a prime requisite for intelligent planning. Understanding the problem makes it possible to decide what effects an attempt should be made to evaluate in the study. Experience has also brought out that experiments when repeated do not often produce the same set of results. By making only a few runs, it is possible to detect first-order or main effects having magnitudes of three or four standard deviations. The smaller the effect to be discovered the greater the number of experimental runs that must be made. If σ_0 is designated as the standard deviation of runs made for a particular treatment combination, then, with 95 percent certainty, effects as large as σ_0 can be measured within $\pm \sigma_0/2$ with 64 runs, effects as large as $2\sigma_0$ can be measured within $\pm \sigma_0$ with 16 runs, and effects as large as $4\sigma_0$ can be measured within $\pm 2\sigma_0$ with four runs.[2] Other criteria for determining the size of an experiment are discussed in statistical textbooks by Kempthrone,[3] Cochran and Cox,[4] and Davies.[5]

Assume that it has been decided that a study will be made of the changes in the purity of some product when temperature, pressure, and acid concentration are each varied from one level to another. Also assume that only eight runs are required to measure large effects with some degree of precision. Then, plans can be made to do the experiment outlined in Table 3, where temperature is factor A, pressure is factor B, and acid concentration is factor C. The eight runs proposed above constitute a 2^3 experiment, a special case of the 2^n class in which n factors each at two levels are considered.

The 2^n Class of Experiments

In the 2^3 experiment, data from the eight runs would make it possible to draw seven conclusions on the effects produced by the variation of three factors. Furthermore, each conclusion can be based on the results from every run. An example of this can be seen from Table 3. Treatment combination abc is the combination of factors in which each factor is at its upper level, but in treatment combination bc, only factors B and C are at their upper levels and factor A is at its lower level. The effects are estimated by comparing the observed values corresponding to two sets of runs. For instance, the A effect is estimated from the observed values for the treatment combinations in which factor A is at the high level and for those combinations in which factor A is at the low level. This estimate can be written as $\frac{1}{4}$ (a + ab + ac + abc — (1) — b — c — bc), where the letters represent the values observed for the indicated treatment. The A × B interaction, or the difference in the A effect at each level of factor B, is estimated as $\frac{1}{4}$ (ac + abc — b — bc — a — ac + (1) + c). Seven such contrasts can be established for a 2^3 experiment. In general, the complete investigation of the effects produced by the variation of n factors from one level to another, in the context of all possible combinations of the other n — 1 factors, would require 2^n runs. The number of main effects and of low-order interactions is listed for several 2^n factorial designs in Table 4.

It can be shown that $(2^n - 1)$ conclusions may be

TABLE 1

RUN	Combination of Factors
1.	(1)
2.	a
3.	b
4.	ab

TABLE 2

RUN	Combination of Factors	RUN	Combination of Factors
1.	0 0 0	10.	1 0 0
2.	0 0 1	11.	1 0 1
3.	0 0 2	12.	1 0 2
4.	0 1 0	13.	1 1 0
5.	0 1 1	14.	1 1 1
6.	0 1 2	15.	1 1 2
7.	0 2 0	16.	1 2 0
8.	0 2 1	17.	1 2 1
9.	0 2 2	18.	1 2 2

TABLE 3

RUN	Treatment Combination
1.	(1)
2.	a
3.	b
4.	c
5.	ab
6.	ac
7.	bc
8.	abc

TABLE 4[1]

EFFECTS	NUMBER OF FACTORS, n						
	2	3	4	5	6	7	8
Main	2	3	4	5	6	7	8
Two-factor interactions	1	3	6	10	15	21	28
Three-factor interactions	..	1	4	10	20	35	56
Four-factor interactions	..	..	1	5	15	35	70
Total number of runs	4	8	16	32	64	128	256

[1] A more extensive table can be found in Reference 6.

drawn from a 2^n experiment. Making all the possible contrasts in a 2^n experiment can be quite cumbersome without a system for the analysis. Such systems, however, are available.

One way of obtaining the seven conclusions from the results of the 2^3 experiment (Table 5) is the placing of the proper values into the appropriate four cells of a series of "2 x 2" tables. Each of the four cells in each "2 x 2" table contains the sum of the two runs that fit the cell specification. The following two-way table is obtained from the data presented in Table 5:

		Factor A	
		Low	High	Total
Factor B				
	Low	14	12	26
	High	15	10	25
	Total	29	22	51

The effect of changing factor A from its low level to its high level is estimated from the difference in the column totals. Similarly, the effect of factor B is estimated from the difference in the row totals. The $A \times B$ interaction effect is estimated from the difference of the diagonal totals. The remaining conclusions are drawn from the two-way tables for factors A and C, for factors B and C, and for factors B and C at each level of A. The $A \times B \times C$ interaction effect is estimated from the data combined in the latter two tables.

Another technique for obtaining the seven conclusions from the 2^3 experiment is illustrated in Table 6.

To evaluate the effects shown in Table 6, the sum of the experimental values for those treatments indicated by a minus sign is subtracted from the sum of the observed values indicated by a plus sign. Dividing the difference by four gives the average effect or contrast. For example, the estimate of the average $B \times C$ effect is $\frac{1}{4}[(6 + 5 + 9 + 7) - (6 + 3 + 8 + 7)] = 0.75$ units. This value should check the $B \times C$ interaction as determined from the two-way tables for factors B and C. Table 6 is easy to construct. For the main effect of any factor, a plus sign is placed opposite each treatment combination in which that factor appears at the high level. The signs under each interaction are the algebraic products of the signs under the corresponding main effects. The construction of Table 6 is covered in greater detail in a number of statistical textbooks.

The third systematic method of obtaining the seven contrasts from the 2^3 experiment is Yates' calculation. This device is presented in Table 7. In this case, the number of columns for completing the numerical process is three. Generally, the number of columns is determined by the exponent n in the 2^n designation. The first half of the entries in Column 1 is obtained by summing succeeding pairs of the experimental values, and the second half of the entries in Column 1 is obtained by determining the differences for these same pairs of experimental values. The first number of the pair is always subtracted from the second number. The remaining columns are constructed in the same manner as Column 1, Column 2 being constructed from the data in Column 1, and Column 3 being constructed from the data in Column 2. The total effects are read directly from the n-th column, and the average effects are then obtained by multiplying the total effects by $\frac{1}{2^{n-1}}$. In the above example, the average effects are one fourth of the total effects.

The first two methods of establishing the effects of the factors become complicated as the value of n in the 2^n experiment increases. Yates' system appears to be simpler for handling the data from larger experiments. Furthermore, Yates' calculations can be checked. The data in each column can be verified before proceeding to the following column. The details of Yates' system and the proper check are found in the textbook by Davies.[5]

Other Experimental Designs

Table 4 demonstrates the rapid increase in the size of the experiment with each increase in n. From the standpoint of economy and practicability, it is obvious that the number of experimental runs becomes prohibitive. Also, the larger experiments provide the investigator with information on high-order interactions that are likely to be negligible and of no interest to him. Thus, it is desirable to plan a smaller experiment. A smaller and more practical experiment can be designed by selecting a fraction of the runs required for a full factorial experiment. It would be well at this time to examine briefly a means of devising fractional factorial experiments.

If it were decided to carry out only eight runs in an experiment that involved four factors each at two levels, it would be necessary to select a balanced set of eight runs from the 16 runs possible. To achieve the smaller experiment, some sacrifice must be made. The estimates of the effects of the factors would not be determined with as high a precision as they would be had the complete experiment been run. Then, too, one half the effects would be inseparable

TABLE 5

Treatment Combination	Hypothetical Test Values
(1)	6
a	5
b	6
c	8
ab	3
ac	7
bc	9
abc	7

TABLE 6

Treatment	EFFECT						
	A	B	C	A x B	A x C	B x C	A x B x C
(1)	−	−	−	+	+	+	−
a	+	−	−	−	−	+	+
b	−	+	−	−	+	−	+
ab	+	+	−	+	−	−	−
c	−	−	+	+	−	−	+
ac	+	−	+	−	+	−	−
bc	−	+	+	−	−	+	−
abc	+	+	+	+	+	+	+

TABLE 7

Treatment	Observed Values	Column 1	Column 2	Column 3	Effect
(1)...........	6	11	20	51	Total
a............	5	9	31	—7	A
b............	6	15	—4	—1	B
ab...........	3	16	—3	—3	AB
c............	8	—1	—2	11	C
ac...........	7	—3	1	1	AC
bc...........	9	—1	—2	3	BC
abc..........	7	—2	—1	1	ABC

TABLE 8

Effect	Alias Effect
A..	BCD
B..	ACD
C..	ABD
AB.......................................	CD
BC.......................................	AD
ABC......................................	D

from the remaining effects; that is, each effect is confounded with another effect. This phenomenon can be observed by referring to Table 6. Suppose the effect of the fourth factor, factor D, is confounded with the A $\times$ B $\times$ C interaction effect, then the aliases, or the effects with which each effect is confounded, can be listed as in Table 8. This means that the main effects are confounded with three-factor interactions and that the two-factor interactions are confounded in pairs. Such a condition may not be serious if an effect or its alias effect is not important.

The aforementioned fractional factorial experiment is one of many such experiments that can be developed. Brownlee, Kelley, and Lorraine,[7] and others[8] have developed practical fractional factorial systems. And recently, C. Daniel[9] reported on a whole set of fractional replicates in which the two-factor interactions are clear. Other designs are also possible; for example, fractional factorial designs (to be reported elsewhere) have been used to evaluate the effect of as many as 16 factors in 32 runs. In these designs, each main effect is estimated free of confounding with all two-factor interactions.

The experimental designs discussed here are by no means the only designs available to the experimenter. Many other plans, too numerous to mention, have been developed by Kempthrone,[3] Cochran and Cox,[4] Davies,[5] and Box.[10]

Interpretation of Experimental Data

The technique most widely used to facilitate the analysis and interpretation of experimental data is the analysis of variance. More-recent developments in multiple comparisons, linear programming, surface fitting, stochastic processes, and extreme-value

theory promise to provide a reservoir of knowledge suitable for application to industrial problems.

Summary

Since all the data obtained can be used in drawing each conclusion, balanced factorial experiments make it possible to draw conclusions of considerable generality. To evaluate the effects of various factors, a simple method of analysis can be applied to the experimental data. Once the effect is estimated, some basis must be used for judging whether the observed changes in responses are real. Recent developments enable the experimenter to make these judgements with a high degree of confidence.

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Мороженое

Question C—Corrosion Mitigation Practice

1. **How your company is combatting corrosion—inhibitors, plastic coatings, alloys, or other means.**

   All companies are using inhibitors. The use of high pump settings was mentioned by some operators as an early solution. One operator stated that his company had installed insulated flanges to eliminate the flow of stray currents.

2. **How many wells are involved—flowing, rod pumping, hydraulic pumping, gas lift?**

   One-thousand and twenty-three rod pumping and 64 hydraulic pumping wells were being treated with inhibitors. No flowing or gas lift wells were treated. From 12 percent to 100 percent of the rod pumping wells operated by each company were being treated.

3. **If you are using inhibitors:**

   a. *What type chemicals are being used (water soluble, oil soluble, etc.) and how many wells of each type are treated?*

   The data reported indicate that 65-75 percent of the wells are treated with oil soluble-water dispersable inhibitors, about 25-30 percent with oil soluble-water insoluble inhibitors, and the remainder with oil insoluble-water soluble inhibitors. In all, some sixteen compounds were reported to be in use at the present with possibly an equal number that have been used successfully in the past. Most of these discontinued compounds were dropped as companies standardized their treating programs.

   Three operators are now using their "own" brand of inhibitors (i.e., compounds developed by their company). Two operators are using a contract service on a portion of their wells (that is, the complete treating program including chemical injection and iron count control is handled by a contractor). Three operators are now using "competitive priced" inhibitors after several years of study. "Competitive priced" refers to inhibitors sold at a low cost to meet competition (usually a "weaker" than standard inhibitor). Several operators are still studying their inhibitor program and are still evaluating inhibitors. Most agreed, however, that nearly any "name brand" inhibitor can be used successfully in East Texas.

   b. *How much chemical is used and on what schedule (one quart per producing day, one gallon per week, or any other)?*

   The amount of chemical and treating schedule varied a great deal, even within the same company. The most common treatments, however, seem to be one to two quarts per producing day or one gallon per week. Several operators use as little as one pint per day in some wells and two operators reported one pint per day as their standard treatment. Six operators reported using weekly treatments and three of these use that schedule exclusively. Most operators who vary the volume of their treatment do so on the basis of fluid production, although there was no agreement as to the proportions required. Several operators are still experimenting with their treating schedules and have not set a policy. Most operators use an initial treatment of five gallons batched down the annulus followed by full well stream circulation.

   c. *How inhibitor is applied (batch treatment down the annulus, continuous treatment, sticks, or other).*

   All operators reported that they are now using batch treatments down the annulus on rod pumping wells. Most follow the batch with a short flush with well fluids to wash the chemical down to the fluid level. Some reported that they follow their batches with full well stream circulation.

   Continuous treatments are used on the hydraulic pumping wells. Several operators have tried continuous treatment on rod pumping wells, but this has been abandoned except for scale prevention treatment. The use of pellets dropped down the annulus have been tried as have the use of sticks dropped when the pump was out of the hole, but neither of these proved too successful.

   d. *When do you start treatment (at first failure, at certain water percentage, or volume, when put on pump, or other)?*

   Equipment failures were the most common criteria reported, inasmuch as excessive failures are also used by those using water production as a criteria. Six operators reported starting treatment on basis of water production. Two operators started when water volumes reached 100 barrels per day, and the others when water percentages reached from 50 to 80 percent. Two operators reported that they had no set policy and two reported starting some treatment on the basis of high iron counts.

   e. *Who in your company decides "a," "b," "c," and "d"?*

   Field personnel, both engineers and producing people have the power to make these decisions in most companies. Recommendations on chemicals and schedules come quite often from the company's laboratory or corrosion section.

   f. *How long has your company been treating in East Texas?*

   Four of the companies have been actively combatting corrosion in East Texas for five years or longer. The remainder have been at it at least two years.

   g. *If available, what dollar value can be placed on treatment? (any costs and economics you can release.)*

   No cost figures were available from most companies, although they expressed the opinion that savings are appreciable. One company did report, however, an average savings of $537 per well per year on 96 wells and another reported savings of $252 per well per year on 91 wells. Two other operators who did not have cost data reported that pulling jobs on their wells had been reduced 70-80 percent and 75-90 percent respectively. Several operators reported that in addition to savings due to reduced rod and tubing failures, the number of rod pump failures had decreased, and that they had been able to use common steel pumps rather than expensive alloy ones. It was mentioned that pump repair shops have complained of the decrease in pump failures since inhibitors were introduced into East Texas. It was also mentioned that the number of well servicing rigs had decreased in the area since inhibition became wide spread.

D. Other information—any special procedures or unique experiences your company has had with East Texas corrosion control (any special approaches that have been tried—and don't forget things that have been tried and have failed).

1. It was reported in some cases that wells that were making very little water (5 barrels of water per day or less) were being treated because of excessive failures.

2. It was reported that many early attempts were made to combat East Texas corrosion by such things as annulus pumping, up hole pump settings, and the use of rod guides, all of which met with little success.

3. One operator reported that his producing people claim that their wells make more oil when extensive full well stream circulation is used after treating.

ATTACHMENT 1—Company Replies to Question A

Question A. Nature and severity of corrosion (how your company feels toward downhole corrosion in East Texas; that is, is it mild or severe, does it present an economic problem, etc.?).

Company "A": At the present we feel that the corrosion in the East Texas Field is not severe as compared to some other fields; however, it does present operational problems and expenses and it can be economically combatted.

Company "B": Feel that corrosion is mild but it is economical to treat high water producers.

Company "C": A serious downhole economic corrosion problem does exist in East Texas.

Company "D": Downhole corrosion appears to be the result of salt water and possibly a small amount of H_2S in certain areas. Some corrosion also may result from currents introduced through flow lines. On a field-wide basis, corrosion is considered very mild. Certain individual wells, usually large water producers, present serious corrosion problems but the problem is believed to be the combined result of corrosion and rod-on-tubing wear. Corrosion in large water wells is considered to be an economic problem.

Company "E": Corrosion is mild to severe in East Texas, depending on area, water production, etc. It very definitely is an economic problem.

Company "F": Company feels that downhole corrosion is not necessarily severe (with respect to some other fields); however, it does present a problem in economics.

Company "G": Nature and severity of corrosion: mild to medium corrosion (8-9 months between pulling jobs for any reason on untreated heavy water wells), but widespread enough so that it is economical to treat wells (three years on wells making 50 percent or under water—about 14 months average over all.)

Company "H": Mild to severe corrosion.

Company "I": Corrosion is not particularly severe; however, it does present an economic problem.

Company "J": We feel that downhole corrosion is severe and presents an economic problem. This problem is becoming more severe all the time.

Company "K": Corrosion mild to severe—economical to treat.

Company "L": Mild but definitely economic. Some measures of control or mitigation are justified.

ATTACHMENT 2—Company Replies to Question B

Question B. Criteria for corrosion and corrosion control (how your company determines extent of problem and success of control, equipment failure histories, cost histories, inspections, coupon studies, iron count, etc.—with any examples you have available).

Company "A": We are presently using equipment failures as criteria, are assembling cost histories, and are currently evaluating applications of iron count methods.

Company "B": Failure histories and water percentages (80 percent water) are used as criteria to start treatment; histories are used for evaluation.

Company "C": Record of well pulling and rod and tubing repair jobs are used. Coupons and iron count are studied.

Company "D": Criteria for corrosion are the case histories of individual wells and their pulling expense. No coupon tests or iron content studies have been made. Success of treatment is determined by decrease of pulling expense.

ATTACHMENT 3—Company Replies to Question C (Corrosion Mitigation Practice)

Company	1. Methods Used	2. Total Wells Involved	3. If you are Using Inhibitors a. What type chemicals are being used? And how many wells of each type are treated?	b. How much chemical is Used? On what Schedule?	c. How Inhibitor Applied	d. Treatment Started	e. Who Decides	f. Years treated	g. Economics
"A"	Inhibitors	37-Rod pump of 305 28-Hydraulic of 28	30-RP: 23 HP: oil soluble-water dispersible. 7-RP: oil insoluble-water soluble. 5 HP: oil soluble-water insoluble (Are still testing several compounds)	Testing and have no set policy. Use 1 qt/ producing day and 2—8 qts/ week Initial—5 gal and circulate	RP: Batch w/30 min flush HP: Continuous into power oil	Most: First failure. Some: Iron count	Corrosion Engineer	2½ years, Present program 1 year	Have not established
"B"	Inhibitors	36-Rod pump treated	36-RP: oil soluble-water dispersible (Now using "competitive" priced inhibitor)	Use 1 pt to 1 qt per 25 BO and per 225 BW (Avg: 1½ qts per day) Initial—5 gal and circulate	Batch daily	At 80% water or on failure	Corrosion Section	2 years	None available
"C"	Inhibitors	50-Rod pump treated	21-RP: oil soluble-water dispersible 29-RP: oil soluble-water insoluble (Are using several compounds)	Use 1 pt per 400 BW Initial—5 gal and circulate	Batch daily	Excessive rod or tubing failures	No policy set yet	2 years	Study not complete
"D"	Inhibitors	73-Rod pump treated of 426 on pump	73-RP: oil soluble-water dispersible (Use "own" inhibitor)	Most now 1 pt/ day Start some at 1 qt/day Initial—5 gal and circulate	Batch daily w/flush of 2 barrel well fluid	At 100 BW PD or excessive failures	Research then field adjusts	Present program 1951	Savings are known to be substantial
"E"	Inhibitors	106-Rod pump treated of 226 on pump	106-RP: oil soluble-water insoluble (Now use "own" inhibitor) (Have used most commercial inhibitors)	Use 1 pt/100-150 bbl/day Avg: 1 qt/day Initial—1 gal/ day for 5 days	Batch daily w/30 min flush	At 80% water or more than 2 failures/ year	Lab—a,b,c; Corrosion Engineer —d	1951	$537/well /year saved on 96 wells
"F"	Inhibitors	82-Rod pump treated of 82 on pump	82-RP: oil soluble-water dispersible. (Now use "competitive" price inhibitor) (Have successfully used several others)	Most: 1 gal/ week Some: 1 qt every other day	Batch daily w/30 min circulation	At 70% water or more than 2 failures/ month	Field Production & Engineering	5–6 years	Pulling jobs reduced by 70–80%
"G"	Inhibitors	114-Rod pump of 400 17-Hydraulic of 65	49-Wells: oil soluble-water dispersible 82-Wells: oil soluble-water insoluble (Are using several compounds)	Most: 1 gal/ week Initial—5 gal and circulate	Batch weekly w/15-30 min circulation	At 100 BWPD	Field Production and Engineering	2½ years	$23,000/ year based on 91 wells making over 100 BWD
"H"	Inhibitors	92-Rod pump 19-Hydraulic treated	?-Wells: oil soluble-water dispersible ?-Wells: oil insoluble-water soluble (Are using contract service on 39 wells)	Originally: 1 qt/ day Now: 1 gal/ week Initial: 5 gal and circulate	Batch w/flush	Failures and equipment inspection	Foreman w/Engineers	2 years	None given
"I"	Inhibitors	30-Rod pump treated	15-RP: oil insoluble-water soluble 15-RP: oil soluble-water dispersible (Are using several compounds)	Most: 1 qt/2nd day and 3 pt twice a week—others: 1 pt/day to 1 gal/week	Batch w/flush	At 50% water	District Supt.	5 years	None available
"J"	Inhibitors	198-Rod pump treated	49-RP: oil soluble-water insoluble 145-RP: oil soluble-water dispersible 4-RP: oil insoluble-water soluble (Are using contract service on 50 wells)	From 1 to 2 gal/ week depending on Iron Count Initial—5 gal and circulate	Batch weekly and and circulate	When iron high when well put on pump	Lab and Field	Present program 2 years	None available
"K"	Inhibitors	147-Rod pump treated	147-RP: oil soluble-water dispersible (Have used many commercial compounds with equal success— now use mostly "competitive")	Varies from 1-2 qts/day to 5-8 qt/week	Batch and flush or circulate ½ to 4 hours	On inspection or on first failure	Foreman Engineers Pumper	Since 1953	Pulling jobs reduced by 75–90%
"L"	Inhibitors	58-Rod pump treated	58-RP: water soluble (Now use "own" inhibitor)	Avg: 1-2 qts/ producing day Initial—1 gal/ day for 7 days	Batch w/ full circulation for 30 minutes to 3 hours	No policy— usually excessive failures	Lab w/ Field Personnel	Since late 1953	Have had definite reduction

Company "E": Criteria for corrosion and its control is based on equipment failure records, water production, and visual equipment inspection. Coupons and iron counts were found to be erratic in results and unreliable.

Company "F": Extent of corrosion problem and success of control is determined from rod and tubing failure reports, or equipment failure histories. Some coupon studies and iron counts have been made; however, they were few and are not generally used. Main criteria is well pulling reports which show type of failure, frequency, material replaced and cost of repairs.

Company "G": Criteria for corrosion and corrosion control is based on incidence of tubing leaks and rod breaks, visual inspections, and tubing surveys. We believe the corrosion occurs throughout all the field and in all wells making any water

and becomes more troublesome as the wells make more water. We have not found evidence that above a certain water-oil ratio the metals become water wet and the rate of corrosion increases. Coupons and iron counts are not used as a basis on which to treat wells. We originally started treating troublesome wells but have extended the program to include all wells making over 100 barrels of water per day and are experimentally trying treating wells with less water at lower dosages to see if we can economically extend the program further. We have not been able to treat wells and evaluate success on an individual basis. Success of control is based on average incidence of tubing leaks or rod breaks and the average tubing wear measured by caliper surveys in a large number of treated wells compared to a large number of untreated wells.

Company "H": We use rod and tubing

failures as criteria and are undecided about water percentage; however we also start treatment at 50 percent water. We use iron count reduction and cost records for evaluation and control.

Company "I": Principal equipment failure histories, inspections and iron count. Coupon studies have been used to a limited extent.

Company "J": Corrosion determined by:
1. Equipment failures histories (pulling job frequency).
2. Visual inspection of downhole equipment.
3. Iron counts.
   Controlled by: iron counts and pulling job frequency curves.

Company "K": Use failure histories as criteria. Make occasional iron counts to check to see if treatment is being applied and is working.

Company "L": Rod and tubing failures. No cost data available.

NACE TECHNICAL COMMITTEE REPORT

Water Dependent Sweet Oil Well Corrosion Laboratory Studies

Reports of NACE Technical Unit Committee T-1C on Sweet Oil Well Corrosion.[1] Compiled by Task Group T-1C-2 On Water Dependent Corrosion, Experimental Aspects.[2]

Introduction

SINCE OCTOBER 1956, Task Group T-1C-2 has been concerned primarily with the relation of characteristics of produced water to subsurface equipment failure frequency. Specifically, an attempt has been made to correlate bottom hole pH, as calculated by the methods of Rogers,[1] to such factors as tubing life (as determined by caliper surveys or well records) under various production conditions.

A data sheet as shown in Table 1 was circulated to members of T-1C. From the replies a number of bottom hole pH values were calculated and the data plotted against expected or observed tubing life. The results appear in Figure 1.

The 65 wells in Figure 1 include 37 flowing wells and 28 gas lift wells. No pumping wells were plotted because of the lack of tubing failure data. The data generally appear to represent a somewhat random scattering. This was not unexpected in dealing with a plot of pH against tubing life with no regard to total water produced or water-oil ratio. However, even under these conditions one fact is rather evident: there are very few wells in the upper left quadrant of the graph, that is, the portion above a 12 year tubing life and below pH 6. This portion is set off by the arrows in Figure 1. By count there are 26 wells which had a bottom hole pH below 6. Only three of these showed tubing lives in excess of 12 years and only 8 were in excess of 9 years. A breakdown of this in percent is shown in Table 2.

Additional inspection of Figure 1 reveals a greater spread of the dots representing flowing wells than of the crosses which represent gas lift wells. In order to clarify this difference each type of well was plotted separately, as shown in Figures 2 and 3. It will be noted also in Figures 2 and 3 that numerical values are associated with each point. The number preceding the slanted bar is the total water produced by the well in thousands of barrels. The number

Abstract

Extensive data are reported to show the correlation between bottom hole pH and tubing life under various production conditions. Data are given to show the following relationships: tubing life to calculated bottom hole pH for flowing gas lift sweet oil wells; tubing life to calculated bottom hole pH for gas lift sweet oil wells; produced iron and bottom hole pH for flowing, gas lift and pumping sweet oil wells, and tubing life and produced iron in gas lift sweet oil wells. Total and average water production also are indicated for certain wells.   8.4.3

following is the average percent water produced in the life of the well.

In Figure 2 an attempt has been made to plot a flexible curve which will encompass the majority of the points recorded. The shaded portion thus represents the average plot of tubing life vs bottom hole pH. By count, 29 of the 37 points lie within or very near to the shaded portion. Of the eight points which are somewhat removed from the curve, six represent wells which have produced an average of less than 30 percent water. The other two have produced about 50 percent water.

The curve indicates a bottom hole pH of 6 ± 0.2 to be somewhat critical in determining the expected tubing life. It will be noted that only one well of six with a pH above 6.2 has a tubing life less than 20 years. The analogy below pH 6 was mentioned in connection with Figure 1.

Examining those points within or adjacent to the shaded portion furnishes additional information of interest. Below pH 5.5 the corrosion rate is generally high regardless of the percent water (at least to a minimum of 1 percent). In fact, to obtain a bottom hole pH below 5.5, it usually is necessary to have a low-water well with a high GOR, unless the water contains excessive quantities of non-volatile acids. These "high pressure sweet oil wells" are of course very closely related to gas condensate wells. From pH 5.5 to 6.0 it will be noted that those wells which have made 40 percent or more water are generally in the lower portion (tubing life 7 years or less) while those below 40 percent water fall in the 8-10
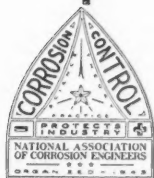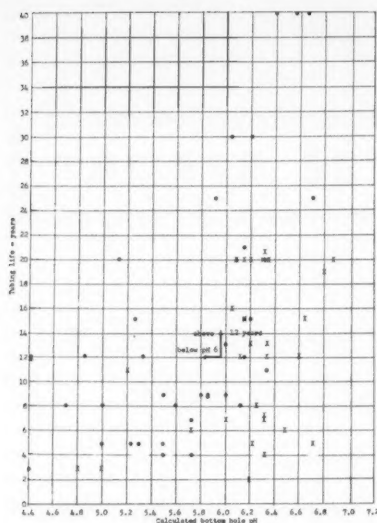
Figure 1—Relation of tubing life to calculated bottom hole pH for flowing and gas lift sweet oil wells. Black dots indicate flowing wells and x's represent gas lifts.
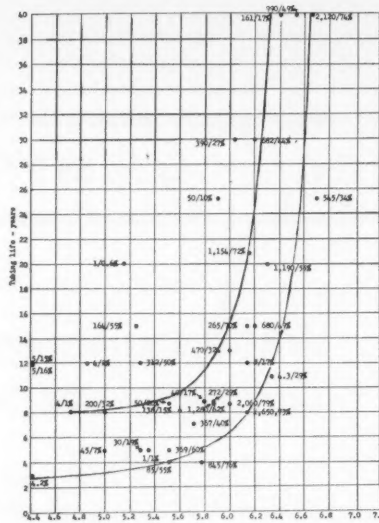
Figure 2—Relation of tubing life to calculated bottom hole pH. Total and average water production is indicated for flowing sweet oil wells. Numbers are in thousands of barrels of water produced/average percent water produced in life of well. For example, the notation 390/27% would mean a well has made 390,000 barrels of water at an average of 27 percent water.
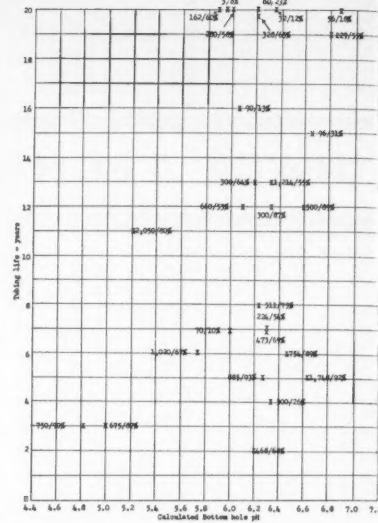
Figure 3—Relation of tubing life to calculated bottom hole pH. Total and average water production are indicated for gas lift sweet oil wells. Numbers are in thousands of barrels of water produced/average percent water produced.
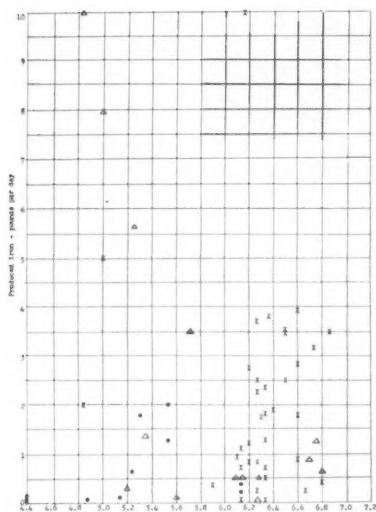
Figure 4—Relation of produced iron to calculated bottom hole pH for flowing, gas lift and pumping sweet oil wells. Black dots represent flowing wells, x's indicate gas lifts and triangles show pumping wells.

TABLE 1
Data for Estimating Bottom Hole pH

WELL DATA	WELL NUMBER 1 2 3 4 5 6
Oil Production (bbls/day)	
Water Production (bbls/day)	
Gas: oil ratio (cu. ft./bbl.)	
Oil Gravity (°API)	
Depth to Perforations (ft.)	
Percent CO_2 in Separator (gas)	
Total dissolved solids in brine (ppm)	
Bicarbonate in water (ppm)	
pH of water at start of bicarbonate titration	
Bottom hole temperature (°F)	
Total oil produced in life of well (bbls)	
Total water produced in life of well (bbls) (estimate if not available)	
Estimated tubing life (flowing or gas lift wells) from caliper survey or replacement records	
Estimated monthly cost (or other basis) due to corrosion	
Average iron counts (ppm or ppd)	
Type Well (F, G/L, P)	

years class. Above pH 6, only one of 13 wells has a tubing life less than 11 years.

Figure 3 represents a corresponding plot of tubing life vs bottom hole pH for gas lift wells. It will be noted that an expanded tubing life scale is used, resulting in a maximum of 20 as compared to 40 in Figures 1 and 2. Actually the wells on the 20 year abscissa were reported as > 20 years. It is obvious that little or no correlation exists between pH and tubing life for the data shown. This may indicate that pH is not the primary factor in gas lift well corrosion. The small number of points (4 of 28) which fall below pH 6 is surprising. This may be due to the fact that an accurate estimate of gas-oil ratio is difficult to obtain on a gas lift well. This ratio is

one of the more critical components of the bottom hole pH calculation; if it is underestimated a considerable increase in pH can result.

Although all four of the points below pH 6 in Figure 3 correspond to tubing lives below 12 years, it is also true that nine of 24 points at pH 6 or above also have tubing lives below 12 years. A more significant correlation is that involving total water and percent water. There are 18 wells with a tubing life of 13 years or less. Only two of these 18 make less than 50 percent water and only three have produced less than 300,000 barrels of water. Conversely of 10 wells over 13 years tubing life, only four have made over 50 percent water and only one has produced in excess of 300,000 barrels of water. The data are not detailed enough to allow a com-

parison of water production per year with tubing life. However, it appears that such a correlation may exist.

In an attempt to establish another criterion for water dependent sweet oil well corrosion, the bottom hole pH data also were compared with pounds of iron produced per day. These points appear in Figure 4. This figure includes pumping wells for which the pounds per day were available. Unfortunately, not many iron counts were available for the flowing wells, and as a result the number of this class in Figure 4 is much less than the number in Figure 1.

An inspection of Figure 4 indicates a random scattering of points for all but pumping wells, which appear to follow a definite pattern. A large number of points for gas lift wells are shown, but as in the tubing life—pH plot, the pattern is random. For a closer inspection of gas lift data the points were replotted in Figure 5. All points fell below 5 pounds per day. The numerical percentages conform to present percent water. This was used instead of the average percent water because the iron per day calculation was based on the present figure. It is obvious that no correlation between pH and iron per day exists. In regard to percent water, it will be noted that only one of 14 wells which produce less than 1 pound of iron per day is making as much as 90 percent water. On the other hand, 14 of 22 wells producing in excess of 1 pound of iron per day make 90 percent or more water. This, however, is a somewhat forced correlation since the pounds of iron are directly related to volume of produced water, which in turn is related to percent water.

The pumping wells, represented in Figure 4 by triangles, appear to come nearest to achieving a pattern. These points are replotted in Figure 6. The numbers are current percent water production again for the reason that the produced iron is calculated from the current figures. It is apparent in Figure 6 that those wells which make over 80 percent water form a smooth curve
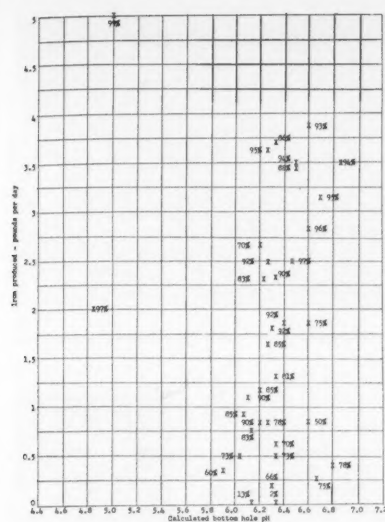
Figure 5—Relation of produced iron to calculated bottom hole pH. Present percent water is indicated for gas lift sweet oil wells. Numbers indicate present percent water.
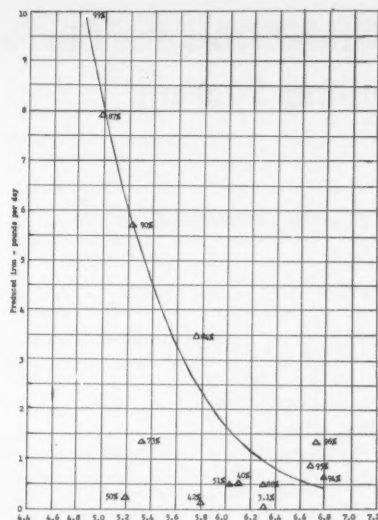
Figure 6—Relation of produced iron to calculated bottom hole pH, for pumping sweet oil wells. Numbers represent present percent water.
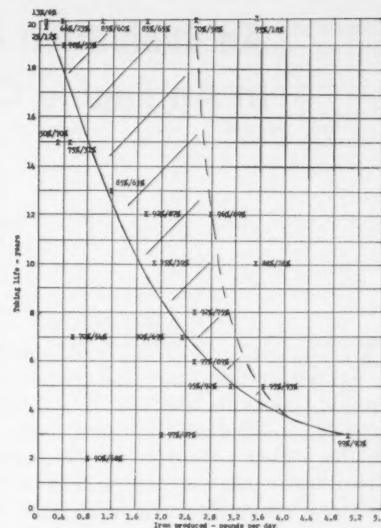
Figure 7—Relation of tubing life to produced iron in gas lift sweet oil wells. Numbers indicate present percent water/average total water percent. For example, 96/89% indicates well is presently making 96 percent water and has made an average of 89 percent water since completion.

TABLE 2—Tubing Life of Wells

Tubing Life	Bottom Hole pH	NUMBER WELLS		
		G/L	F	Total
> 12 years	<6	0	3	3
12 years or less	<6	4	19	23
% 12 years or less	<6	100%	86%	89%
> 9 years	<6	1	7	8
9 years or less	<6	3	15	18
% 9 years or less	<6	75%	68%	69%

which shows a rather sharp increase in iron below a pH of 6. Conversely, several wells with a bottom hole pH below 6 and a water percentage below 80 percent are relatively low in iron production. The difference here is far greater than would be attributed to the amount of water produced alone. The corresponding well repair cost data are not complete but it can be said that several of the low pound per day wells which have pH values below 6.4 are high corrosion cost wells ($5-$10 per day). The three wells above pH 6.6 are low cost wells despite their high water percentage.

Since no correlation was found between produced iron and bottom hole pH in gas lift wells, it was decided to plot tubing life vs pounds of iron for these wells. The points are shown in Figure 7. In this case the first number represents the current percent water and the number after the slanted bar the average percent water for the life of the well. As mentioned previously, the current percent water relates directly to the pounds of iron produced. The average percent is noted as a comparison with the current percent.

In Figure 7 most of the points fall along the solid line. The dotted line and the corresponding shaded portion represent an inclusion, for the most part, of the > 20 year tubing life points at the top abscissa. The well corresponding to the upper right hand point probably now has a shortened tubing life

expectancy due to the sudden change in produced water percent. The three wells with short tubing lives in the lower left corner are less easily explained since water production in these wells is typical of the group. For the remaining points it appears that a tubing life below 10 years may be expected if the pounds per day of produced iron averages 1.6 to 2.8 or more. This will be especially true if the percentage and volume of water are also high.

Summary

The foregoing figures are based on a relatively small quantity of data, and thus it is not the intention of this task group to make specific predictions at this time. However, the observed trends may be recorded as follows:

1. A calculated bottom hole pH below 6.0 in gas lift and flowing sweet oil wells indicates that a tubing life of 12 years or less can be expected. Conversely, above pH 6 in flowing wells a tubing life above 12 years can be expected.

2. Below a bottom hole pH of 5.5 in flowing sweet oil wells, the tubing life can be short at water percentages as low as 1 percent.

3. From a bottom hole pH of 5.5 to 6.0 those flowing wells making 40 percent or less water appear to fall in the 8-10 year tub-

ing life range. Above 40 percent water in this pH range the tubing life is generally below seven years.

4. No correlation between tubing life and bottom hole pH in gas lift sweet oil wells is apparent at this time.

5. Those gas lift wells which have produced over 300,000 barrels of water and over 50 percent water have tubing lives below 13 years. Those gas lift wells which have produced less than 300,000 barrels of water at a ratio below 50 percent have tubing lives in excess of 13 years.

6. No correlation is evident between bottom hole pH and pounds per day of produced iron for gas lift wells.

7. Pumping sweet oil wells making in excess of 80 percent water show a sharp increase in produced iron as the pH drops below 6.0.

8. Pumping sweet oil wells with a bottom hole pH below 6.0 can fall in the $5-$10 per day corrosion cost range at water ratios as low as 40 percent.

9. Pumping sweet oil wells above pH 6.6 appear to be low corrosion cost wells even at 95 percent water.

10. Gas lift sweet oil wells show a correlation between pounds per day of produced iron and tubing life. Wells in the 1.6-2.8 pounds per day range can be expected to have tubing lives below 10 years.

Reference

1. W. F. Rogers. *Corrosion*, 12, No. 12, 595-601t (1956) Dec.

An Evaluation of Inhibitors for Corrosion Prevention In An Engine Cooling System*

By LEONARD C. ROWE

LEONARD C. ROWE—Senior Research Chemist, Chemistry Dept., Research Staff, General Motors Corp. He holds a BS (1943) and MS (1947) from Michigan State University. He is active in corrosion activities for GMC and presently is chairman of its corrosion committee. He is a member of ACS and of NACE Unit Committees T-3A and T-4D. In addition he is a member of NACE Detroit executive committee and correspondent for the Transportation Industry for Corrosion.

Introduction

VARIOUS INHIBITORS have been recommended for corrosion prevention in an engine cooling system. The use of chromates, nitrites, benzoates, and borates represent only a few which have had a rather extensive investigation.[1,2,3] Experience has shown that presently used reliable winter antifreezes are sufficiently well inhibited to give corrosion-free service in the majority of cases when used as directed. Therefore, this investigation was not initiated to recommend a specific inhibitor but to assist in determining reasons for failure in isolated cases and to serve as a basis for inhibitor selection should aluminum metal become prevalent in a cooling system.

The factors influencing the process of corrosion in a multi-metal engine cooling system are many-fold. These factors have been discussed in detail by other authors[4,5] and the brief itemization which follows will serve to emphasize the scope which is involved.

a. Coolant flow

b. Aeration

c. Operating temperatures

d. Water composition variables

e. Corrosion by-products

f. Antifreeze characteristics

g. Couples of dissimilar metals

h. Exhaust gas leakage into coolant

i. Metal hot spots

j. Metal stresses

k. Operating conditions

Since the variables involved in a laboratory test must be limited to some degree, it was the intent to encompass as many as possible through the use of several tests. On this basis the study was made as a three part investigation. (1) Rotating specimen test to evaluate inhibitor effectiveness for each metal, (2) Galvanic couple tests, and (3) The use of an inhibitor combination, based on the results of (1) and (2), in a laboratory model of an engine cooling system.

Rotating Specimen Test

Test Conditions

The degree of corrosivity, caused by coolant waters, depends upon the source which may be tap, well, or surface water.[6] To include a greater scope of corrosive conditions, the following solutions were

Abstract

The variation of coolants used in a multi-metal engine cooling system offers a challenge for corrosion inhibition. The diverse characteristics of this system are discussed along with their relationship to the selection of laboratory test methods to investigate inhibition.

A rotating specimen type of test is used for the evaluation. The effectiveness of inhibitors, such as sodium borate, sodium nitrite, sodium benzoate, potassium dichromate, soluble oil, and sodium mercaptobenzothiazole, is compared by means of this test. Various test media are used, including ethyleneglycol-water mixtures and tap water with and without additional corrosive constituents. The metals investigated are steel, copper, brass, aluminum, cast iron and solder. The results are based on corrosion rate, microscopic examination, pit depth when applicable, and other general examinations.

This work includes the results of one year static room temperature tests on thirteen galvanic couple combinations for each inhibitor.

Based on the results obtained by conventional corrosion tests, a final examination of a combination of inhibitors is made in a laboratory model which simulates an engine cooling system. This test indicates effective inhibition by this combination in a system using either a copper-brass or aluminum radiator.

4.6.4

selected to test individual metals with and without the presence of an inhibitor.

a. Detroit tap water

b. Test water (i.e., Detroit tap water plus 2 grams/liter of sodium chloride and a gram/liter of sodium sulfate.)

c. Ethylene glycol and Detroit tap water (1:1).

d. Ethylene glycol and Detroit tap water (1:1) plus 2 grams/liter of sodium chloride and 1 gram/liter of sodium sulfate.

The addition of chlorides and sulfates simulated an extreme condition of a corrosive water that might
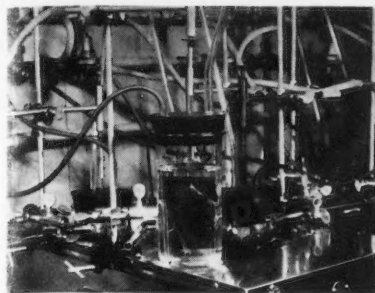
Figure 1—Rotating specimen test apparatus.
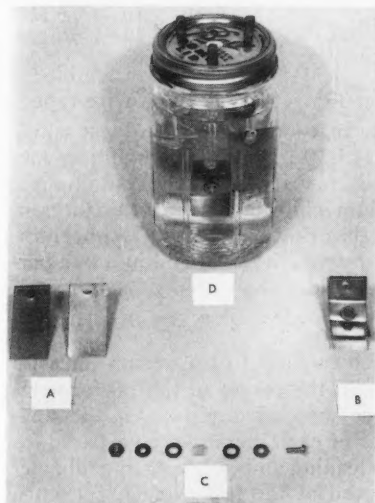
Figure 2—Galvanic corrosion test apparatus.

TABLE 1—A Comparison of Inhibitor Effectiveness in the Prevention of Metal Corrosion[1]

Metal	Solution[2]	INHIBITOR						
		None	Sodium Borate	Sodium Nitrite	Sodium Benzoate	Potassium Dichromate	Soluble Oil	Sodium Mercapto-benzo-thiazole
Steel.........	a	140	<1	0	<1	0	1	<1
	b	510	355	0	4	1	<1	365
	c	460	<1	<1	<1	<1	<1	<1
	d	465	255	<1	250	<1	<1	200
Brass.........	a	<1	<1	<1	1	<1	7	<1
	b	1		8	5	3	2	<1
	c	4	1	1	16	<1	2	<1
	d	108	33	1	71	<1	2	<1
Copper.......	a	1	3	3	1	1	2	<1
	b	3	3	14	11	1	2	1
	c	13	3	3	12	<1	1	<1
	d	185	45	20	169	<1	3	<1
Aluminum....	a	0	4	<1	<1	<1	3	13
	b	<1	15	<1	1	<1	2	10
	c	<1	5	1	1	<1	<1	<1
	d	3	7	1	3	<1	<1	<1
Cast Iron.....	a	101	<1	1	91	2	<1	36
	b	98	144	3	107	2	1	109
	c	70	<1	1	52	1	<1	12
	d	82	79	2	55	1	8	47
Solder........	a	2	1	7	1	2	16	<1
	b	10	1	8	1	1	20	<1
	c	14	2	26	5	1	37	3
	d	12	10	19	16	<1	24	4

[1] Corrosion rate in milligrams per square decimeter per day.
[2] Solution a—Tap water.
   b—Tap water plus 2 gms/liter of $NaCl$ and 1 gm/liter of Na_2SO_4.
   c—Ethylene glycol—tap water (1:1).
   d—Ethylene glycol—tap water (1:1) plus 2 gms/liter of $NaCl$ and 1 gm/liter of Na_2SO_4.

be used as a coolant. The fifty percent glycol solution was selected as representative of the maximum use of this type antifreeze.

The following type and size of metal specimens were used in these tests.

Aluminum, Type 3003	$2'' \times 4'' \times .030''$
Steel, SAE 1010	$2'' \times 4'' \times .035''$
Copper, electrolytic	$2'' \times 4'' \times .020''$
Brass, (Cu-70, Zn-30)	$2'' \times 4'' \times .030''$
Cast Iron	$1\frac{1}{4}''$ diameter disc $\times$ .128''
Solder, (Pb-70, Sn-30)	3'' of .120'' wire type

The tests were run in duplicate at a temperature of 170 F $\pm$ 2 degrees F for a period of 14 days. The volume of the solution was 750 milliliters. The solution was constantly aerated to maintain saturated conditions at the testing temperature. The metal specimen was rotated at 100 rpm $\pm$ 10 rpm. One percent of the inhibitor was used, based on weight if a solid or volume if a liquid. Reagent grade chemicals and inhibitors were used with the exception of soluble oil and sodium mercaptobenzothiazole (Mbt) which were commercially available as inhibitors. Ethylene glycol was a technical grade material.

Apparatus and Procedure

Metal specimens were solvent cleaned and lightly scrubbed with pumice prior to final rinsing and dry-ing. Steel samples were abraded with No. 120 emery paper prior to cleaning. Copper and brass specimens were dipped in 20 percent hydrochloric acid to remove any oxide layer. All specimens were stored in a desiccator for one hour before weighing.

The test apparatus is shown in Figure 1. The metal specimen is held by a glass holder which is connected to an air jet stirrer. Air is passed into the stirrer and flows from jets, causing the stirrer to rotate. The resultant rotation of the metal specimen through the solution takes the place of solution flow past the metal. The solution is aerated by passing air through a piece of glass tubing with a small orifice at the outlet. An air condenser is sufficient to condense vapors from the test vessel. The test container is kept in a constant temperature water bath to maintain the solution at the desired temperature. A group of the test apparatus was established to accommodate 16 tests at one time.

Heavy corrosion products were removed from tested metals by scraping or scrubbing with a brush. Ferrous metals were electrolytically cleaned in a 5 percent sulfuric acid solution, Rhodine inhibited, at 165 F. Copper and brass were given a one minute immersion in 20 percent hydrochloric acid, followed by light brushing. Corrosion products were removed from aluminum with a 2 percent chromic acid and 5 percent phosphoric acid solution at 175 F. Solder specimens were cleaned in a 10 percent acetic acid solution for 5 minutes at a temperature just below boiling. Blank determinations were made in triplicate for these cleaning procedures to be used as a correction for weight loss figures.

Evaluation of Tests

In evaluating a particular inhibitor the corrosion

rate was compared to that of a metal without inhibition. Microscopic examinations were used as an aid to visual examination. Other points which were considered are as follows:

  a. Condition of the metal—discoloration, roughening, general corrosion, and corrosion products.

  b. Pits—size and location.

  c. Condition of the liquid—cloudiness, precipitate, and color.

  d. pH of the solution before and after the test.

Results

On the basis of corrosion rates the results of individual tests are shown in Table 1. It is evident that each of the six inhibitors was fairly effective in the tap water and fifty percent glycol solutions. The presence of the chloride and sulfate ions in the other solutions produced a decided loss in the efficiency of inhibitors such as sodium borate, benzoate, and mercaptobenzothiazole. Sodium nitrite, potassium dichromate, and soluble oil must be considered as providing the best overall inhibition for all metals. The good inhibiting qualities of nitrites and dichromates or chromates have been verified by other investigators[7,8] and is only further substantiated by these results. Dichromate inhibitors cannot be recommended for glycol solutions because of the resultant sludge formation which occurs in the reduction of the chromium ion. This reduction was undoubtedly hastened by light exposure since no attempt was made to exclude sunlight from the test area.

Although only minor corrosion rates are shown for aluminum, specimens were pitted in the glycol-test water solutions which had either no inhibitor or sodium borate or benzoate. Soluble oil produced a very fine network of shallow grooves on the surface of aluminum in both water solutions. Sodium mercaptobenzothiazole had a tendency to form a yellow precipitate on the metal surface which might account for the formation of pinpoint pits over the aluminum surface.

The type of corrosion which developed with chloride and sulfate additions to inhibited solutions resulted in deep grooving and pitting of the metal or, in the case of brass, dezincification. This type of corrosion could lead to eventual perforation which would mean complete failure in a cooling system.

Although there were some increases in the corrosion rate of solder in the presence of sodium nitrite, these were not of major proportions. The greatest increase in the corrosion rate of solder can be observed with the use of soluble oil. This corrosion was so general that no visible change in appearance of the metal surface could be observed.

If there is no buffering action, the tendency of ethylene glycol solutions is to become acidic through oxidation, accelerated by heat. This change in pH is more predominant in the presence of some inhibitors and must be considered in an evaluation. Table 2 indicates the general trend in pH change over the test period. The pH of some solutions increased,

presumably due to the conversion of bicarbonates to carbonates.

Galvanic Couple Test

This test was devised to determine the effect of inhibition in bimetallic contacts. Due to the magnitude of the tests involved, only the most practical combinations were attempted.

Test Conditions

The following type and size of metal specimens were used in these tests.

Aluminum, Type 1100	$2'' \times 1'' \times .030''$
Steel, SAE 1010	$2'' \times 1'' \times .035''$
Copper, electrolytic	$2'' \times 1'' \times .020''$
Brass, (Cu-70, Zn-30)	$2'' \times 1'' \times .030''$
Cast Iron	$1\frac{1}{2}''$ diameter disc $\times .128''$
Solder, (Pb-70, Sn-30)	$3''$ of $.120''$ wire type

The test was a static, room temperature test which had a test duration of 10 months. The solution consisted of 800 milliliters of tap water, containing 2 grams/liter of sodium chloride and 1 gram/liter of sodium sulfate. Inhibitors were used at a concentration of one percent by weight if a solid and one percent by volume if a liquid.

Apparatus and Procedure

The test container consisted of a mason jar with a one-half inch hole in the center of the lid for aeration. Specimens were suspended midway in the solution. Two specimens of each metal were prepared for each test. Prior to cleaning and weighing, one-quarter inch holes were placed at the top of each specimen for hanging and one-quarter inch holes in the centers of those which were to make the couple. After weighing, one specimen of each metal to be tested was

TABLE 2—Trend in pH Change of Various Inhibited Solutions Over a Fourteen Day Test Period

Inhibitor	Solution	Initial pH	Final Average pH[1]
None	a[2]	7.5	8.4
	b[3]	7.5	8.1
	c[4]	7.4	5.4
	d[5]	7.5	5.2
Sodium Borate	a	9.1	9.1
	b	9.1	9.1
	c	7.4	7.2
	d	7.4	7.2
Sodium Nitrite	a	7.7	8.3
	b	7.6	8.2
	c	7.2	7.8
	d	7.3	7.8
Sodium Benzoate	a	7.8	8.5
	b	7.6	8.4
	c	7.6	6.7
	d	7.4	6.0
Potassium Dichromate	a	5.0	5.2
	b	5.0	5.1
	c	6.2	6.4
	d	6.1	6.5
Soluble Oil	a	8.4	8.9
	b	8.3	8.8
	c	8.3	8.3
	d	7.8	7.5
Mercaptobenzothiazole	a	9.1	8.7
	b	9.0	8.8
	c	9.5	8.5
	d	9.5	8.7

[1] Based on the average pH from five solutions and each contained a different metal.
[2] Solution a—Tap water.
[3] Solution b—Tap water plus 2 gms/liter of NaCl and 1 gm/liter of Na₂SO₄.
[4] Solution c—Ethylene glycol—tap water (1:1).
[5] Solution d—Ethylene glycol—tap water (1:1) plus 2 gms/liter of NaCl and 1 gm/liter of Na₂SO₄.

attached together giving a metal to metal contact. Metals were attached with a brass bolt, nut, and insulating washers. The bolt was covered with Koroseal tubing to prevent metal contact. When both of the metals in the couple were of the sheet type, the front piece had the upper and lower third of the specimen bent at a 45 degree angle. This permitted the observation of part of the metals not in tight contact.

Each test container contained a couple of the two metals and individual specimens with no contact. Figure 2 shows (a) individual specimens, (b) couple, (c) materials for insulating and connecting couple, and (d) complete test arrangement. When assembled, the containers were placed aside for periodic observations. Monthly additions of tap water were made to maintain the solution level with as litle disturbance to the solution as possible.

Results

The results of these tests are given in Tables 3, 4 and 5, based on loss in weight of the metal. In the case of aluminum, metal perforation or deep pitting often occurred and would not be readily apparent from the graphs. For this reason data are included in Table 6 on the maximum pit depth for aluminum. Pit depth measurements were made with a constant pressure micrometer. One other case of metal pitting was serious. In the presence of the Mbt inhibitor, steel was perforated when coupled and uncoupled with cast iron. Penetration of more than two-thirds the metal depth occurred when steel was tested with copper and brass in the presence of Mbt.

Although the results obtained are indicative of what might happen under similar conditions, they can only be accepted as comparative and to offer possible dangerous combinations. Variations can occur with change in medium, temperature, metal composition, etc. In many cases the addition of an inhibitor increased the rate of attack of the metal or changed the galvanic tendency of the couple. This was particularly true in the case of aluminum.

TABLE 3—A Comparison of Inhibitor Effectiveness in the Prevention of Galvanic Corrosion of Aluminum Couples[1]

| Metal | None | INHIBITOR | | | | | |
		Sodium Borate	Sodium Nitrite	Sodium Benzoate	Potassium Dichromate	Soluble Oil	Sodium Mercapto-benzo-thiazole
Aluminum...	43	330	59	54	0	121	34
Copper.....	20	10	25	26	2	51	2
*Aluminum..	166	570	577	343	46	143	83
*Copper.....	0	0	1	1	0	7	3
Aluminum..	48	296	54	43	0	91	9
Brass......	95	4	19	161	4	47	2
*Aluminum..	109	601	633	174	20	136	40
*Brass......	1	0	1	1	1	16	2
Aluminum...	35	204	50	26	1	21	190
Steel.......	782	739	0	630	2	1	459
*Aluminum..	18	386	564	15	17	177	293
*Steel......	574	21	12	528	10	10	15
Aluminum...	31	196	44	33	1	15	169
Cast Iron...	555	740	0	603	0	11	366
*Aluminum..	24	332	394	36	61	167	226
*Cast Iron..	374	12	6	465	0	17	7
Aluminum..	38	154	43	44	0	20	6
Solder......	4	1	40	6	2	4	0
*Aluminum..	39	262	76	67	7	15	5
*Solder......	2	1	12	0	0	4	0

[1] Total weight loss is expressed in milligrams.
* Galvanic couple.

TABLE 4—A Comparison of Inhibitor Effectiveness in the Prevention of Galvanic Corrosion of Brass and Steel Couples[1]

| Metal | None | INHIBITOR | | | | | |
		Sodium Borate	Sodium Nitrite	Sodium Benzoate	Potassium Dichromate	Soluble Oil	Sodium Mercapto-benzo-thiazole
Brass......	76	21	10	74	3	20	2
Steel.......	815	749	0	565	3	20	547
*Brass......	2	0	18	0	1	10	4
*Steel......	860	1161	4	830	199	35	482
Brass......	65	20	23	74	3	16	2
Cast Iron...	522	599	1	504	1	13	421
*Brass......	1	0	12	1	2	11	3
*Cast Iron...	823	872	28	797	211	26	316
Brass......	53	20	24	14	9	15	3
Solder......	3	1	637	4	1	4	0
*Brass......	2	16	3	9	8	12	2
*Solder......	163	41	1473	19	5	9	1
Steel.......	680	658	0	586	3	1	410
Cast Iron...	490	475	0	581	0	21	343
*Steel......	666	211	25	581	11	3	365
*Cast Iron...	50	511	39	88	4	20	101

[1] Total weight loss in milligrams.
* Galvanic couple.

TABLE 5—A Comparison of Inhibitor Effectiveness in the Prevention of Galvanic Corrosion of Copper Couples[1]

| Metal | None | INHIBITOR | | | | | |
		Sodium Borate	Sodium Nitrite	Sodium Benzoate	Potassium Dichromate	Soluble Oil	Sodium Mercapto-benzo-thriazole
Copper.....	55	16	24	43	4	29	3
Steel.......	750	732	0	612	6	1	510
*Copper.....	1	0	18	0	0	7	3
*Steel.......	919	1113	211	870	73	12	454
Copper.....	12	6	13	9	3	25	4
Brass......	9	12	16	10	6	30	2
*Copper.....	6	7	10	6	9	23	3
*Brass......	28	18	33	22	9	18	2
Copper.....	70	13	32	47	3	6	3
Cast Iron...	572	579	8	538	0	11	419
*Copper.....	2	0	16	1	1	5	3
*Cast Iron..	849	872	228	817	106	13	307
Copper.....	15	6	33	9	3	14	2
Solder......	8	1	652	2	3	6	1
*Copper.....	3	8	8	6	10	9	3
*Solder......	138	26	714	32	7	12	1

[1] Total weight loss in milligrams.
* Galvanic couple.

Specific details can be obtained from the tables with regard to individual metals, couples, and inhibitors. The following general remarks can be made for each inhibitor. Sodium borate is satisfactory for copper, brass, and solder but unsatisfactory for aluminum, steel, and cast iron. Sodium nitrite is satisfactory for steel, cast iron, copper, brass, solder in the absence of copper and brass, and uncoupled aluminum. It is unsatisfactory for coupled aluminum and solder in the presence of copper and brass. Sodium benzoate is satisfactory for copper, brass, solder, and fair for aluminum but unsatisfactory for steel and cast iron. Potassium dichromate is satisfactory for copper, brass, solder, cast iron, steel, and fair with aluminum. It is only fair for steel and cast iron when in contact with copper and brass. Soluble oil is satisfactory for copper, brass, steel, cast iron, and solder but unsatisfactory for aluminum. Sodium mercaptobenzothiazole is satisfactory for copper, brass, and solder but unsatisfactory for aluminum, steel, and cast iron.

Laboratory Model Engine Cooling System Test

In order to simulate conditions in an automotive cooling system, a laboratory model was designed and built. The complete assembly is shown in Figure 3. It consists of a small cast iron block with a passageway for the coolant. A pair of strip heaters under the block heats the block externally and permits heating of the coolant through the block. The remainder of the system consists of a small radiator and a pump. Rubber hose connections are used from radiator to pump, pump to block, and block to radiator. The temperature is maintained by thermostatic control in the block and a fan type blower on the radiator. An attempt was made to maintain the major metal ratios as closely as possible to that in a conventional system.

Test Conditions

The comparative wetted surface areas between the actual cooling system and that of the model are as follows:

	Actual[9]	**Model**
Cast Iron	1652.5 sq. in.	92.0 sq. in.
Brass (including thermostat)	52.6 sq. in.	*
Steel	12.7 sq. in.	—
Zinc (plated)	5.3 sq. in.	—
Rubber	210.5 sq. in.	*
Radiator	2900.0 sq. in.	160.0 sq. in.

Two liters of a 1:1 mixture of ethylene glycol and water were used as the test solution. This solution was circulated for eight hours per day during the five day week at a temperature of 180 F. The test was left in a static condition at room temperature for the remainder of the test period. Uninhibited solutions were tested for a total time of three weeks and inhibited for six weeks. The inhibitor solution com-

* Brass fittings and rubber tubing were used in the system but no attempt was made to maintain exact ratios.
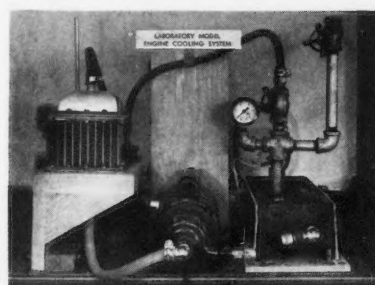
Figure 3—A laboratory model of an engine cooling system for inhibitor testing.

TABLE 6—Maximum Pit Depth of Aluminum (inches) After Galvanic Tests

Inhibitor	METAL COMBINATIONS				
	Aluminum-Copper	Aluminum-Brass	Aluminum-Steel	Aluminum-Cast Iron	Aluminum-Solder
None					
Uncoupled	......	......	......	.0110	......
Coupled	.0173	.0211	......	......	.0045
Borax					
Uncoupled	Pe*	Pe	Pe	Pe	Pe
Coupled	Pe	Pe	Pe	Pe	Pe
Sodium Nitrite					
Uncoupled	.0024	.0014	......	.0030	.0015
Coupled	Pe	Pe	Pe	.0154	.0043
Sodium Benzoate					
Uncoupled	.0093	.0093	.0086	.0119	.0051
Coupled	Pe	.0197	......	......	.0081
Potassium Dichromate					
Uncoupled	......	......	......	......	......
Coupled	.0192	Pe	.0102	.0208	.0055
Soluble Oil					
Uncoupled	Pe	Pe	.0172	.0123	......
Coupled	Pe	Pe	Pe	Pe	.0102
MBT					
Uncoupled	......	......	.0015	......	......
Coupled	.0058	Pe	.0292 (Pe)	Pe	......

* Pe—Metal Perforated.

bination that was used in these tests consisted of 0.5 percent soluble oil, 0.3 percent of an aqueous solution containing fifty percent sodium mercaptobenzothiazole, and 0.2 percent of sodium nitrite.

Procedure

The test solution was prepared prior to introduction into the system. The system was allowed to come to operating temperature before turning on the fan at the radiator. The test cycle, as specified under test conditions, was followed for the necessary period of time.

At the conclusion of the test period the block, pump, and radiator were disassembled for inspection. A sample of the coolant was retained for a pH measurement. A sample of the corrosion products was taken from the block for analysis. The various parts of the assembly were cleaned, and the model reassembled with a new radiator and hose sections for the next test.

Results

Originally the test was started as a closed system with a moderate pressure of three pounds. A copper-
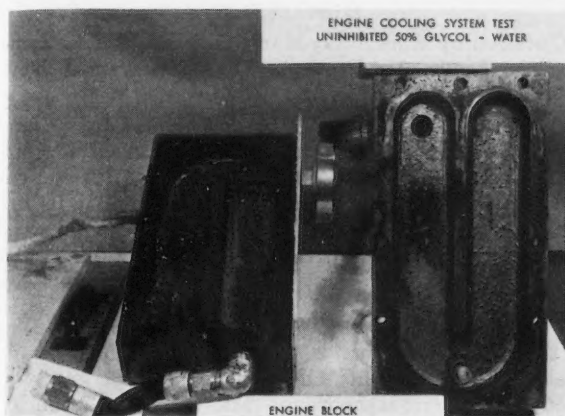
Figure 4—Engine block after three-week test with uninhibited 50 percent ethylene glycol-water solution.

Figure 5—Engine block after six-week test with inhibited 50 percent ethylene glycol-water solution.

brass radiator was used with no inhibitor in the solution. The pH of the glycol-water solution was 7.0. Over a three week period the pH dropped to 6.7, indicating little glycol breakdown to acidic compounds. The pressure was moved to 9 pounds for one week. This did not accelerate the glycol breakdown. The radiator developed small leaks and solution additions had to be made to the system. This sporadic testing was continued for three months when the assembly was disassembled and inspected.

It was observed that relatively little corrosion had taken place in the engine block. There was a thin layer of rust with a slightly higher accumulation on the upper half of the passage way. The pH of the solution was 5.9. This would tend to indicate that in the pressurized systems used today there is less corrosion taking place and the glycol breakdown is not as rapid.

An air chamber was introduced into the system. The chamber consisted of a one liter lipless beaker which was stoppered. A one-half inch hole permitted exposure to the atmosphere. The coolant returned to this chamber with sufficient force to produce violent agitation. The test was repeated under these conditions. At the end of three weeks the pH had dropped to 4.6 and the test was discontinued. The accumulation of corrosion products and the effects of corrosion can be observed in Figure 4.

The degree of corrosion was evident from the rusty color and sludgy appearance of the coolant. The corrosion products consisted of a heavy, gummy material which had accumulated to a depth of one-quarter to one-half inch in the block. There was no stoppage of radiator tubes although an excess of rust was apparent. Rusting of the pump section was evident and some minor blade wear had taken place.

The test was repeated with an inhibited solution and a new radiator. The pH of the inhibited solution was 9.5 at the beginning of the test. After six weeks of testing or twice as long as with the uninhibited solution, the pH had dropped to 8.25. The results of the test may be observed in Figure 5. Most of the interior parts had a thin coating of rust. This could be due to some residual rust that was left in inaccessible lines after the last test. The passageways of the radiator were cleaner than those in the previous test. The pump had a slight rust deposit. There was a slightly heavier deposit of rust on the top and outlet side of the block. The solution was a straw yellow color. There was no evidence of a heavy oil layer in the system.
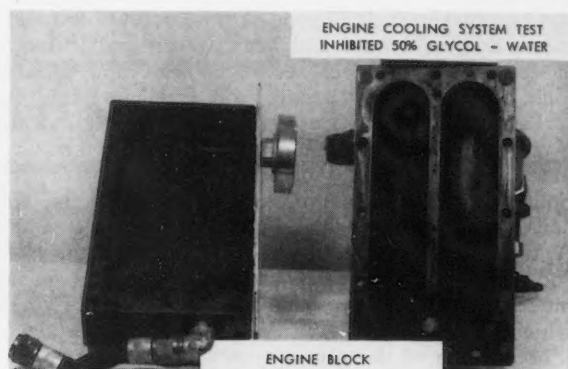
A repetition of the tests, using aluminum radiators, produced results very similar to that in which the copper-brass radiator was used. At the conclusion of the uninhibited test the pH of the solution was 4.4. The aluminum radiator could be termed satisfactory since the corrosion was not too severe. There was more general corrosion of the bottom tank than the upper. The block contained a layer of corrosion products in the lower section and black to brown dry corrosion products in the upper section. There appeared to be some graphitization of the cast iron and the pump blade.

At the conclusion of the inhibited test with the aluminum radiator the coolant had a pH of 8.6. There was a thin film of rust over most of the surfaces. The bottom of the radiator was much cleaner than the top tank. Some darkening of the aluminum occurred in isolated areas. A slightly higher accumulation of dry corrosion products appeared on the top section of the block. Pump and block assemblies were very similar to those shown for the previous test. No pitting of solder or other metals was encountered.

Spectographic and some wet chemical analyses were made of the corrosion deposits which were removed from the block. In no case was a metal from the system completely absent from the deposits. No direct comparison of inhibition can be obtained from such analyses since a small fraction of the deposit was used in one case and the entire amount in the other. An analysis of the coolants used with the aluminum radiators indicated 15.9 ppm of aluminum in the uninhibited coolant and none in the inhibited coolant.

Conclusions

Although many differences exist among inhibitors, the best inhibitor or combination of inhibitors must be selected on the basis of usefulness for an engine

cooling system. The results of the tests indicate that sodium nitrite is superior for ferrous metals such as steel or cast iron. It is good with aluminum in most cases. Sodium borate and benzoate are particularly susceptible to the presence of chloride and sulfate ions. Potassium dichromate is an excellent inhibitor for most metals but is not compatible with ethylene glycol solutions. Sodium mercaptobenzothiazole, Mbt, is an excellent inhibitor for brass and copper. Soluble oil is a fine inhibitor for most metals but does rather poorly with aluminum in couple tests. A combination inhibitor of soluble oil, Mbt, and sodium nitrite effectively reduces corrosion in a model engine cooling system over a period of time which is twice as long as that necessary to produce a breakdown of the glycol type solution without an inhibitor.

Sodium nitrite is usually considered a poor inhibitor in the presence of solder since it tends to accelerate the corrosive attack of the solder. Although the data in this report indicate a greater corrosion rate of solder in the presence of nitrite, it has been observed that this occurs mainly in the presence of copper metal in the same system. This corrosive effect was not observed in the engine cooling test due to the presence of sodium nitrite in the inhibitor combination.

The type of soluble oil used in these tests produced satisfactory results, but it is known that many differences exist between the various oils. Therefore, individual testing should be done before a particular type is selected for use.

Although an attempt was made to approximate service conditions in these tests, the usefulness of an inhibitor system in the prevention of corrosion can be conclusive only after field testing.

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DISCUSSION

Question by Robert W. Martel and Eugene A. Zientek, Linde Air Products Co., Tonawanda, New York:

It was established that vigorous aeration of an unpressurized and uninhibited glycol-water solution increased corrosion and glycol breakdown. Is the reduction in corrosion and glycol breakdown in the pressurized system attributed to less aeration or to the pressure effect on the chemical reactions in the system?

Reply by Leonard C. Rowe:

Glycol breakdown is rate-dependent upon available oxygen and heat if we disregard the catalytic effect of certain contaminants. The limitation of available oxygen was felt to be the rate reducing agent of glycol breakdown and corrosion. There may be a pressure effect on the chemical reactions, but this was not studied at that time.

Question by Harry H. Redlich, Painesville, Ohio:

It is known that potassium dichromate will oxidize the ethylene glycol in an antifreeze mixture. Do you know any antioxidant which could be added to the antifreeze mixture to prevent this oxidation?

Reply by Leonard C. Rowe:

We have had no experience nor did we investigate the use of an antioxidant to prevent the oxidation of ethylene glycol with potassium dichromate.

Question by A. J. Eickhoff, National Lead Company Research Labs., Brooklyn, N. Y.:

What alkali is most suitable for adjusting pH in automotive cooling systems?

Reply by Leonard C. Rowe:

Sodium borate has been used for years to adjust the pH in an automotive cooling system. Organic or inorganic phosphates or other alkaline materials may be used successfully if they do not form insoluble products. One should not depend upon a pH adjustment to prevent corrosion. Degradation products of ethylene glycol and corrosion products may continue to promote corrosion even though the pH is properly adjusted. When starting with a fresh solution of ethylene glycol, it is desirable that a proper pH be attained. Reserve alkalinity is sometimes established as a criterion for a non-corroding coolant, but I do not believe that this indicates a good inhibited coolant as many of your better inhibitors offer little alkalinity.

Any discussions of this article not published above
will appear in the December, 1957 issue.

NACE TECHNICAL COMMITTEE REPORT

Corrosion by Acetic Acid

A Report of Task Group T-5A-3
On Corrosion by Acetic Acid[1]

Introduction

Scope

NACE Technical Practices Committee 5A-3 on Corrosion by Acetic Acid was established to correlate information on the corrosion problems involved in the manufacture, storage and transport of relatively pure acetic acid solutions. The committee has made no attempt to consider the complex corrosion problems involved in the handling of acetic acid solutions above their normal boiling point or in mixtures with other corrosive chemicals. However, as even relatively pure acetic acid solutions are considered border line cases of passivity for many materials of construction, the effect of minor impurities must be considered in the proper choice of materials for many acetic acid services.

It is the purpose of this report to present the combined experience of leading producers and users of acetic acid and suppliers of metals and alloys for acetic acid service. Laboratory corrosion test results, field corrosion test results, operating experience and typical failures by corrosion in acetic acid are presented.

Much of the corrosion test data presented in this paper is conflicting due to the presence of unreported minor contaminants, emphasizing the importance of testing under field service conditions prior to selection of materials for acetic acid service. Laboratory corrosion test results in acetic acid solutions frequently fail to correlate with service experience and extreme caution should be used in extrapolating laboratory test work to plant scale operations.

Acetic Acid

Acetic acid is produced by the oxidation of acetaldehyde, oxidation of ethanol, fermentation of alcohol, or the destructive distillation of wood. Depending on the method of manufacture, acetic acid may contain traces of formic acid, butyric acid, esters, aldehydes, sulfates, sulfites, chlorides and minor amounts of oxidizing or reducing agents which may materially affect the corro-

Abstract

A summary of data and experience on the use of various materials of construction for the storage and handling of refined glacial acetic acid and dilute acetic acid, submitted to NACE Technical Practices Committee 5A-3 is presented. Discussion of common corrosion problems, laboratory and field corrosion test results and photographs of common types of failure are included.

Aluminum alloy or austenitic stainless steel tankage is recommended for the storage of refined glacial acetic acid. Austenitic stainless steel heating coils, pumps, valves and piping are recommended for both glacial and dilute acetic acid storage systems. The corrosion risk involved in the use of aluminum for dilute acetic acid storage is emphasized and the limitations on the use of copper and copper alloys for acetic acid storage are discussed.

The importance of minor contaminants and of the oxidizing or reducing nature of the environment is discussed in relation to choosing the proper materials for construction of acetic acid processing equipment. It is pointed out that the austenitic stainless steels and copper and copper alloys satisfactorily meet most of the acetic acid processing conditions though higher alloys or non metallic materials may be required occasionally. Common corrosion problems encountered in acetic acid processing and control measures for such problems are discussed.   4.4.2

sion resistance of the common metals and alloys.

Acetic acid is commonly marketed as glacial (over 98 percent) and as 80-85 percent, 56 percent and 28 percent water solutions for use in the manufacture of cellulose acetate, acetate plastics, acetic anhydride and in the textile processing industries.

Early production of acetic acid in this country was by processes such as wood distillation which were essentially reducing in nature and ideally suited to the copper and wood process equipment and tankage available to industry during this period. Much of this copper process equipment and wood tankage is still in use today after 20-30 years service. With the production trend to oxidation processing and development of the aluminum industry, more and more aluminum came into common use for both process equipment and storage facilities.

Development of the austenitic stain-
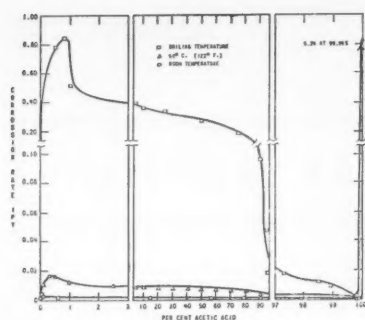
Figure 1—Effect of concentration and temperature on the resistance to corrosion of 1100-H14 aluminum alloy in acetic acid.

TABLE 1—Laboratory Test of 3003 Aluminum in Acetic Acid; Storage Conditions, 105 F, 5000 Hrs.

Acid Concentration	Corrosion Rate, IPY
15%	0.010
80%	0.006
99.5%	0.001

TABLE 2—Laboratory Test of 1100 Aluminum in Boiling Acetic Acid Solutions, 82 Days*

Acid Concentration Percent	Corrosion Rate, IPY
5	0.48
10	0.42
19	0.42
33	0.41
48	0.36
57	0.31
71	0.22
90	0.004
99.5	0.006

* M. G. Fontana Ind. & Eng. Chem., Vol. 40, No. 7, 1948.

less steels has, however, provided the acetic acid industry with the most versatile group of alloys to meet the complex corrosion problems and pressure conditions encountered in the production of acetic acid solutions. Occasionally, corrosion problems arise which cannot be solved by use of these three basic classes of materials and higher alloys such as Worthite, Hastelloy C, 20-class stainless steel and non metallics such as Karbate and Haveg find limited use.

Summary

The data and experience presented in this report can be summarized as follows:

1. The preferred materials of construction for ambient temperature storage of refined glacial acetic acid are:
   Tanks and Tank Cars: Aluminum 1100, 3003, 5052 and 5154
   Heating Coils: Type 316 stainless steel
   Piping: Type 316 stainless steel
   Valves and Pumps: Type 316 stainless steel

Type 316 stainless steel has been recommended for maintaining maximum purity of the acetic acid. Where small amounts of turbidity or color pickup can be tolerated, Type 304 stainless steel may be used successfully.

2. The preferred materials of construction for ambient temperature storage of

pure dilute (less than 90 percent) acetic acid solutions are:
   Tanks and Tank Cars: Type 304 stainless steel
   Piping: Type 304 stainless steel
   Valves and Pumps: Type 316 stainless steel

Where storage of contaminated acid or storage at elevated temperature is required, Type 316 stainless steel is preferred.

3. The choice of materials for process equipment is dependent on the temperature requirements, presence of contaminants and on the oxidizing or reducing nature of the environment. The austenitic stainless steels, Types 304 and 316, or the copper and copper base alloys, will satisfactorily fulfill the requirements of the majority of acetic acid services.

4. Careful attention to design, quality of materials, condition of heat treatment and surface finish, fabrication technique and cleanliness can materially reduce the possibility of corrosion attack on all materials intended for acetic acid service.

5. Minor impurities and the oxidizing or reducing nature of the environment control the corrosion of most common materials in acetic acid service. These variables are incompletely defined in most laboratory or field corrosion test results and in the common materials selection charts and tables. Extrapolation of such data to operating acetic acid processes is difficult and should not be relied on to replace actual field corrosion testing of various materials under the exact environmental conditions they are expected to withstand.

Aluminum and Aluminum Alloys

Glacial Acetic Acid Solutions—Storage

The relatively pure aluminum and aluminum-magnesium alloys, 1100, 3003, 5052 and 5154 are the most commonly used and economical materials for construction of tanks and tank cars for storage of pure glacial acetic acid solutions at normal temperatures. The higher strength, magnesium containing grades such as 5154 have an economic advantage over the purer aluminum alloys such as 3003 in larger storage tanks and in pressurized storage systems. As glacial acetic acid solidifies at 16.6 C, heating facilities are frequently provided in such storage tanks.

The corrosion rate of aluminum in glacial acetic acid, which normally contains 0.1 to 0.2 percent water, does not increase with temperature. Glacial acetic acid which approaches the anhydrous condition can cause severe corrosion of aluminum alloys at high temperatures as shown in Figure 1. Types 304 and 316 stainless steel normally are used for heating coils where metal wall temperatures may be high. Such coils do not require insulation from the aluminum tankage as galvanic corrosion resulting from the stainless steel-to-aluminum couple in glacial acetic acid is rare.

While aluminum and aluminum alloy pipe lines, pumps and valves are used commonly in glacial acetic acid storage systems, their service life is reported to be shorter than for similar materials used as tankage. For this reason, many acetic acid users prefer Type 304 or Type 316 stainless steel for storage system auxiliaries. The decreased service life of aluminum auxiliaries in acetic acid service is due primarily to:

1. High metal wall temperature of piping adjacent to steam tracing lines.
2. High liquid velocities.
3. Dilution of the glacial acid film remaining on pipe walls in emptied but unwashed systems by atmospheric moisture. Aluminum is more rapidly attacked by dilute acetic acid solutions than by concentrated solutions as illustrated in Table 1 and Figure 1.
4. Exterior corrosion of aluminum lines due to the galvanic coupling of copper steam tracing lines to aluminum piping under moist insulation or conditions of moisture condensation.

Stainless steel valves, pumps and lines commonly are coupled to aluminum equipment with no evidence of galvanic attack in glacial acetic acid solutions.

Dilute Acetic Acid Solutions—Storage

Aluminum and aluminum alloys have been extensively used in the textile industry for storage facilities of acetic acid solutions down to 80 percent concentration. However, a number of failures of such aluminum tankage in the storage of 80 percent to 84 percent acid have been reported and the use of aluminum for storage systems on acid concentrations of less than 90 percent acetic acid should be approached with caution. Failures in some instances have been traced to contaminants introduced with dilution waters.

Process Equipment

The use of aluminum or aluminum alloy process equipment, stills, condensers, lines, valves, etc., has been limited to acetic acid concentrations above 98 percent at temperatures at or near the boiling point and to lower temperatures at more dilute acid concentrations. As acid dilution increases and temperatures increase, the corrosion rate of aluminum increases rapidly to rates approaching 0.5 ipy at 5 percent acid concentration and boiling temperatures as indicated in Table 2. Corrosion of aluminum is severe in boiling anhydrous acetic acid, further limiting the usefulness to a narrow range of process conditions.

The successful use of aluminum in acetic acid process equipment is highly dependent on the purity of the solutions being handled. Susceptibility of aluminum alloys to corrosive attack in acetic acid solutions is increased greatly by inorganic halides or reducing acids and reducing organic acids, esters and aldehydes normally encountered in the production and use of acetic acid. Due to the narrow range of processing conditions which can be handled successfully by aluminum and aluminum alloys, they have been replaced largely by the austenitic stainless steels in modern acetic acid processing equipment.

Common Corrosion Problems

Laboratory and field corrosion test data on the corrosion of aluminum and aluminum alloys in acetic acid solutions is presented in Tables 1, 2, 3, 4 and 5. It should be emphasized that such data are applicable only to the exact conditions of the test in question. They cannot be extrapolated successfully to other process conditions or substituted for field testing of the materials which may be used in process equipment. Such data seldom include all of the many variables, such as minor contaminants, which in large measure control results.

Comparison of corrosion rates in the various tables for similar test conditions of temperature and pressure will show a wide variation.

Performance of aluminum in acetic acid solutions is dependent partially on the degree of aeration or presence of oxidizing agents which tend to maintain or repair breaks in the oxide film on aluminum. Oxidizing inhibitors, including small quantities of sodium dichromate, nitric acid and phosphoric acid, may be effective in controlling the corrosion of aluminum in acetic acid solutions.

The corrosion products of aluminum in acetic acid are white and, for this reason, aluminum is used frequently where color contamination cannot be tolerated. Turbidity increases may result from long term storage and transport of glacial or dilute acetic acid solutions. Figure 2 shows the corrosive attack of glacial acetic acid on the side walls of aluminum tank cars after long service. Mild pitting attack of tank bottoms is common also.

Serious pitting attack can result from the presence of metallic mercury in acetic acid solutions so the use of mercury thermometers or pressure regulating systems which might blow metallic mercury directly into the system should be avoided.

Completely anhydrous acetic acid is reported to be severely corrosive to aluminum at boiling temperatures. However, at normal storage temperatures, corrosion rates of high assay (low water content) commercial acid does not appear to be appreciably greater than for normal commercial acetic acid. Table 3 gives comparative corrosion rates for high and low assay acetic acid on aluminum 5154 under storage conditions.

Because small amounts of acetic anhydride, 0.5 to 10 percent, in acetic acid can cause severe corrosion of aluminum and aluminum alloys at boiling temperatures, the addition of water to control corrosion by dilution of the anhydride under these circumstances often is an effective inhibitor. Heavy metal salts, such as copper and mercury acetates in the concentrations normally encountered

in commercial glacial acid do not cause any significant increase in the corrosion of aluminum storage vessels. High chlorides in acetic acid solutions increase the susceptibility to attack.

Use of copper or chromium alloys of aluminum, such as 2000 and 7000 series in acetic acid service is limited. These materials have higher corrosion rates than pure aluminum or magnesium aluminum alloys under most service conditions. Table 4 gives a comparison of the corrosion rates of various aluminum alloys in 70 percent acetic acid at 105 F.

Tank Failures Reported

A number of aluminum tankage failures have been reported by the textile industry in the storage of 80-84 percent acetic acid solutions. Unless past experience or extensive field testing have shown satisfactory performance of aluminum, its use in acetic acid concentrations of less than 90 percent should be approached with caution. Original investigation of these failures indicated the presence of mercury on the tank walls which had failed by severe pitting in the liquid area.

Failure was blamed on high mercury content of the acetic acid. Analysis of the acetic acid failed to show abnormally high heavy metal concentrations. Investigation of the aluminum storage tanks and tank cars handling glacial acetic acid, from which the dilute acid was derived, showed no similar attack. Laboratory tests were conducted on aluminum alloys in acetic acid solutions to which large additions of mercury and copper salts had been made. These tests failed to duplicate the severe attack noted on the failed tankage (Table 5). It is now felt that the failures resulted from normal moderate corrosion rate of aluminum in dilute acetic acid solutions accelerated by impurities, such as high chloride content, of the diluting water.

Reported failures were handled in varying manners, including revolving horizontal cylindrical tanks 180 degrees around their horizontal axis to obtain additional life available in the unattacked top half of the tanks. In some cases, the pitted areas were built up with weld deposits or spray metallizing. Where attack had not been severe, many textile plants realized the economic advantage of purchasing and storing glacial acetic acid and diluting it as their needs required. Tanks which previously had been attacked in dilute acid showed no further attack after storage glacial acid.

Aluminum and aluminum alloy tankage for acetic acid solution is subject to pitting attack under deposits and, in many cases, extended service life of such tankage be obtained by regular cleaning.
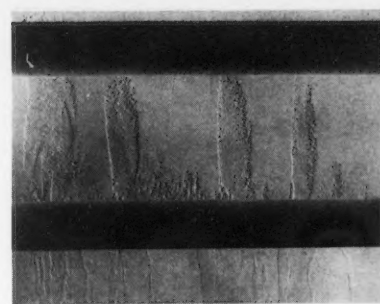
Figure 2—Pitting attack on an aluminum 3003 tank car in glacial acetic acid service.

COPPER AND COPPER ALLOYS

Glacial and Dilute Acetic Acid—Storage

Deoxidized copper, silicon bronze and aluminum bronze are used successfully for storage of both dilute and glacial acetic acid solutions, particularly where storage conditions are neutral or reducing in nature and color pickup by the acid is unimportant. Uninhibited zinc containing copper alloys is subject to severe dezincification in acetic acid solutions and its use for piping, valves, pumps, etc. should be avoided.

Corrosion of copper and copper alloys in the acetic solutions is not primarily a factor of either temperature or acid concentration but is most dependent on the degree of aeration of the acid being handled. Note Table 6. Thus, acid solutions of all concentrations can be stored at temperatures from room to boiling if proper reducing conditions are maintained. However copper ions in glacial acetic acid give a disproportionately high green color due to copper complexes which may be undesirable for some purposes.

Processing Conditions

Copper and copper alloys at one time were the principal materials of construction for process equipment in the production and use of acetic acid, particularly during the period when acetic acid was extensively produced by reducing rather than oxidizing processes. Large quantities of this copper equipment are still in use after 10 to 30 years' service.

In the production and use of acetic acid, four general environmental conditions are encountered commonly in which:

1. Neither copper alloys or austenitic stainless steels are seriously attacked. Such environments may be classified as neutral with respect to oxidizing conditions.
2. Copper and copper alloys are resistant to corrosion while the austenitic stainless steels are severely attacked. These environments are classified as reducing

TABLE 3—Laboratory Test: 5154 Aluminum in Glacial Acetic Acid Under Storage Conditions, 105 F High Assay vs Low Assay Acid, 1000 Hours

Acid Concentration		Corrosion Rate, IPY
Low assay acid		0.00001
High assay acid		0.00010
Low assay acid:	Acetic acid — 99.60%	
	Formic acid — 0.01% (Less than)	
	Acetaldehyde — 0.014%	
	H_2O — 0.38%	
High assay acid:	Acetic acid — 99.95%	
	Formic acid — 0.01% (Less than)	
	Acetaldehyde — 0.002%	
	H_2O — 0.04%	

TABLE 4—Laboratory Test: Aluminum Alloys in 70% Acetic Acid, 105 F, Shaking Rack, 100 Hrs.

MATERIAL	Corrosion Rate, IPY
1100	0.0064
3003	0.0066
5052	0.0059
6061	0.0099
Type 316 S.S.	0.0004

TABLE 5—Laboratory Corrosion Test: Corrosion of 3003 Aluminum in Acetic Acid at 70 C 100-200 Hours Exposure

Percent HAc	Contaminant Added	Corrosion Rate, IPY	Remarks
100.0	None	0.0001	No visible pitting
100.0	1 percent acetic anhydride	0.2218	Etched, pitted
95.4	1 percent acetic anhydride	0.0146	Etched, pitted
89.8	None	0.0245	Pitted
85.0	None	0.0277	Pitted
80.4	None	0.0293	Pitted
80.0	5 ppm metallic mercury	0.0323	Pitted
80.0	5 ppm mercuric acetate	0.0307	Pitted
80.0	5 ppm ferric acetate	0.0258	Pitted
80.0	5 ppm cupric acetate	0.0350	Pitted
70.6	None	0.0249	Pitted
60.0	None	0.0311	Pitted

Figure 3—Air-acid interface attack on deoxidized copper bubble caps.
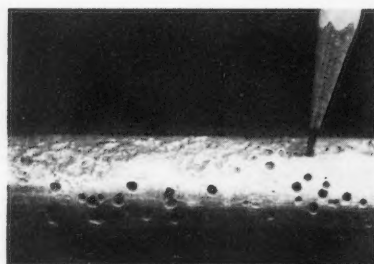
Figure 4—Pitting attack on Admiralty tubing.

Figure 5—Stress corrosion cracking of Admiralty tubing.

Figure 6—Thermal expansion stress cracking of aluminum bronze still.

Figure 7—Layer dezincification of Muntz metal hold down clip.

Figure 8—General attack on hot first pass of Type 316 tube sheet with unattacked Admiralty tubing.

in nature, due to the presence of other organic acids, sulfuric acid or reducing organic compounds.

3. Copper and copper alloys are severely attacked while the austenitic stainless steels are free from general corrosion. Such environments are aerated or oxidizing in nature.

4. Both copper alloys and austenitic stainless steels are subject to corrosion. Such conditions prevail when the environment is either highly oxidizing, as in the presence of chromic acid, or under fluctuating oxidizing and reducing conditions.

Normally it is impossible to estimate the oxidizing or reducing capacity of a process stream from analysis of the stream, nor is it possible to reproduce exactly these conditions on a laboratory scale. Only field exposure of corrosion test racks in operating equipment can gauge adequately the suitability of copper alloys for any given application in acetic acid.

Common Corrosion Problems
1. General Attack

As has been noted previously, general attack on copper alloys in acetic acid solutions is a function primarily of the degree of aeration. Severe attack of copper alloy tankage at the liquid level line is common. This type of attack can be minimized by:

　a. Use of inert gas padding.

　b. Operation of the tanks completely full to avoid air space above the acid.

　c. Operation of the tankage to vary the liquid level, thus spreading the corrosion over a relatively large area and avoiding highly localized attack. Figure 3 illustrates the severe corrosion that can occur at an acid-air interface in copper equipment. This deoxidized copper bubble cap distillation column had operated without difficulty for a number of years in continuous acetic acid service. A period of reduced de-

mand resulted in a period of intermittent operation. The trays were not equipped with weep holes and improper wash down of the tower prior to putting it in standby condition resulted in acetic acid standing on the trays. Very severe corrosion of the bubble caps and down comers occurred in relatively short time at the air-acid interface.
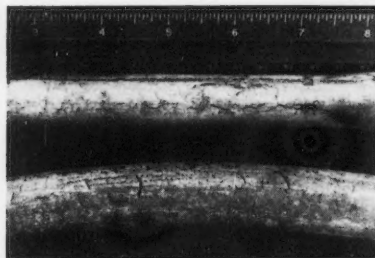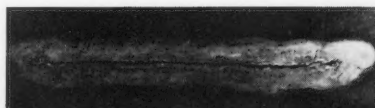
This type of failure can be controlled by continuous operation or, in the case of shutdown, by proper washing, draining and neutralizing of the surface. Control of general corrosion of copper in acetic acid solutions has been attempted by use of inert gas injection, reducing gas injection and oxygen scavengers. Hardness is a factor also in the corrosion resistance of copper and it once was common practice to "hand hammer" the surface of finished copper vessels to insure uniform surface hardening. Thus, annealed areas in copper equipment, due to welding or brazing, sometimes are preferentially attacked. Low zinc alloys are favored in the brazing of copper alloys for acetic acid service.

2. Pitting and Crevice Corrosion

Pitting attack on copper alloys in acetic acid solutions is common, particularly under porous deposits of foreign matter, in areas subject to the high velocity effects of impingement and erosion and in crevices such as that formed under the baffles in tubular heat exchangers. Pitting type of attack on copper alloys is illustrated in Figure 4.
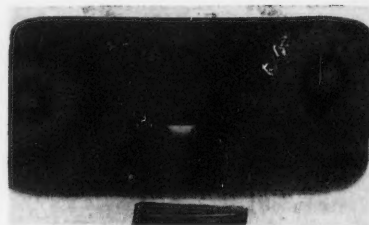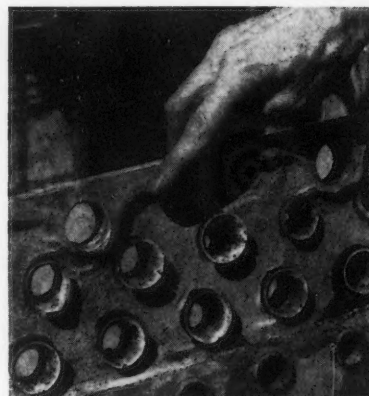
Pinhole leaks and seepage of acid through porous welds are also common in copper acetic acid equipment. The acid leaking to the exterior becomes aerated. Serious corrosion of the exterior of copper vessels and rapid enlarging of the original pinhole leaks can occur unless immediate steps are taken to seal off or repair such leaks.

3. Stress Corrosion Cracking and Corrosion Fatigue

Contamination of acetic acids streams by ammonia or mercury can result in stress corrosion cracking of copper alloys, particularly those containing zinc and subject to either high residual or operating stresses. Such cracks frequently are intergranular in nature and do not show the effects of work hardening usually noted in the transgranular cracks typical of corrosion fatigue failure resulting

TABLE 6—Laboratory Test: Corrosion of Copper in Acetic Acid Solutions, 5-20 Hours

Percent Acid Concentration	Temperature °F	Aeration	Corrosion Rate, IPY
5	Room	None	0.0015
5	Boiling	None	0.0035
7.2	72	N_2 purge	0.0016
7.2	72	N_2 + 10.4% O_2	0.0034
7.2	72	N_2 + 16.1% O_2	0.0063
7.2	72	N_2 + 24.5% O_2	0.0095
50	Room	O_2 purge	0.0715
50	Room	H_2 purge	0.0031
50	Boiling	Immersed	0.0074
50	Boiling	Vapor	0.0109
80	Room	Tank top	0.0209
80	Room	Tank base	0.0109
Glacial	Room	O_2 purge	0.0019
Glacial	Room	H_2 purge	0.0019

4. Stress Cracking

Cracks resulting from pure stress as differentiated from stress corrosion cracking are fairly common in the high strength copper alloys. Figure 6 shows a thermal expansion crack of an aluminum bronze acetic acid column which required early replacement due to the inability to repair such cracks without inducing further cracking. Subsequent investigation by the supplier indicates that this failure may have been a form of stress corrosion cracking subject to control. Publication of the work on the mechanism and control of such cracking is expected in near future. Careful attention should be paid to the high coefficient of expansion of copper alloys in the design of copper alloy vessels and to the hot short characteristics of silicon bronze when this material is used.

5. Dezincification

Both plug and layer types of dezincification are common on copper alloys in acetic acid service and the use of properly inhibited (arsenic, antimony or phosphorous treated) brass is highly recommended. Layer type dezincification of a Muntz metal hold down clip from an acetic acid tower is illustrated in Figure 7.

6. Galvanic Attack

Copper and copper alloys are commonly coupled to stainless steels, as in admiralty tube-stainless steel tube sheet condensers, in acetic acid streams without experiencing difficulty from galvanic corrosion. Figure 8 illustrates such a condenser where the Type 316 stainless steel tube sheet has suffered general attack in the hotter first pass, while the admiralty tubes are unaffected. There is no evidence of galvanic corrosion between the tubes and tube sheet. Galvanic attack is possible between the copper alloys and steel in dilute acetic acid streams but because steel itself is unsuitable for most acetic acid services, such failures are not common.

Figure 9 illustrates such a misapplication where a copper tube bundle was coupled to a steel shell and tube sheet in a condenser for methyl ethyl ketone, ethyl acetate, and water at 210 F. It is believed that the ethyl acetate hydrolyzed to small amounts of acetic acid causing high general corrosion rates on the steel surfaces but accelerated at the points of galvanic contact with the admiralty tube bundle.

Austenitic Stainless Steels

Glacial Acetic Acid Solutions—Storage

Types 304 and 316 stainless steels have been used frequently for acetic acid storage systems where the presence of organic impurities, chlorides, heavy metal salts, high temperatures, high velocities or introduction of moisture to the system have limited the use of aluminum equipment. Typical corrosion rates at normal storage temperatures are given in Table 7 and indicate virtually no attack on these materials in refined acid.

Molybdenum bearing Type 316 stainless steel is preferred for use at temperatures above 150 F or where its increased latitude in resistance to minor contaminants may be warranted. Thus Type 316 stainless steel will be less likely to give increases in acid turbidity where metal wall temperatures may be high, as in heating coils or steam-traced lines. Intergranular attack of the austenitic stainless steels in refined glacial

Figure 9—Galvanic attack on steel shell and tube sheet coupled to Admiralty tube bundle.

acetic acid is not common even at elevated temperatures. Stainless steels for use in acetic acid service should meet the standard ASTM requirements for composition and heat treatment. The use of stabilized grades, such as Types 321, or 347, or post fabrication heat treatment, seldom is warranted.

Dilute Acetic Acid Solutions—Storage

Type 304 stainless steel is the most economical material for tankage, pipe lines, pumps and valves used for dilute acetic acid storage and transport where color contamination or turbidity increases cannot be tolerated. At elevated temperatures, or where the presence of impurities, including chlorides, inorganic or organic, acids, or reducing contaminants are known to cause difficulty, Type 316 is preferred. Table 4 illustrates the superiority of Type 316 stainless steel over aluminum alloys for dilute acetic acid storage at slightly elevated temperatures.

Processing Conditioners

AISI Type 304 and 316 stainless steels, meeting ASTM quality specifications, in the hot rolled, annealed and pickled condition and fabricated by good welding practices, are the most commonly used materials for acetic acid process equipment. Type 304 stainless steel is satisfactorily used in all acetic acid concentrations up through glacial so long as temperatures are relatively low and the acid solutions uncontaminated by reducing compounds. Table 7 illustrates the suitability of Type 304 in acetic acid solutions at low temperature while Table 8 illustrates the increase in rates normally encountered at boiling temperatures.

Intergranular attack of stainless steel seldom is encountered in pure acetic acid solutions and the stabilized grades of stainless steel have only limited us. Where minor contaminants may lead to intergranular attack, the extra low carbon grades of Types 304 or 316 stainless steel generally are preferred over stabilized grades because of their superior general resistance (note Table 8), lower cost and freedom from knife line intergranular attack.

Selection of Materials

1. 400 Series Stainless Steels

The straight chromium stainless steels of the 400 series occasionally show up well in laboratory tests in dilute acetic acid solutions as in Table 9. Field experience with these materials indicates their susceptibility to high corrosion rates and
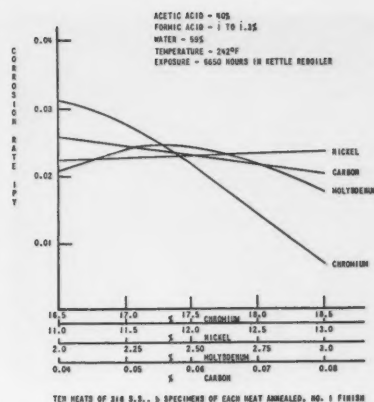
Figure 10—Effect of analysis on corrosion resistance of Type 316 stainless steel in acetic acid solutions: Multiple curvilinear regression statistical analysis of components Cr, Ni, Mo and C.

TABLE 7—Field Corrosion Test in Acetic Acid; Storage at 86-95 F; Stainless Steels*

MATERIAL	Corrosion Rate, IPY	
	24% Acid, 115 Days	98% Acid, 157 Days
Type 304	0.0001	0.0001
Type 316	0.0001	0.0001
Type 317	0.0001	0.0001

* H. O. Teeple, Corrosion, Vol. 8, No. 1, 1952.

TABLE 8—Field Corrision Test, Boiling 99 + % Acetic Acid; Stainless Steel, 21 Days*

MATERIAL	Corrosion Rate, IPY
Type 304	0.018
Type 321	0.047
Type 347	0.041
Type 308	0.053
Type 310	0.039
Type 316	0.0006

* H. O. Teeple, Corrosion, Vol. 8, No. 1, 1952.

TABLE 9—Laboratory Corrosion Test: Corrosion of AISI Type 430 S.S. in Acetic Acid Solution, 45-500 Hrs.

Temperature	% HAc	Corrosion Rate IPY
Room	100	Nil
100 C	100	0.018
Boiling	100	0.024
Room	20	Nil
100 C	20	Nil
Boiling	20	Nil

pitting attack limit their use for acetic acid production equipment. AISI Type 304 stainless steel is the lowest grade commonly used.

2. 18% Chromium—8% Nickel Stainless Steels. AISI Types 304, 304L, 321 and 347 Stainless Steels

These alloys find their greatest range of usefulness in relatively pure acetic acid streams at moderate temperatures. As with all stainless steels intended for acetic acid service, careful attention should be paid to maintaining high quality standards in both materials and fabrication. Such steels should be used only in the annealed condition prior to fabrication and should meet
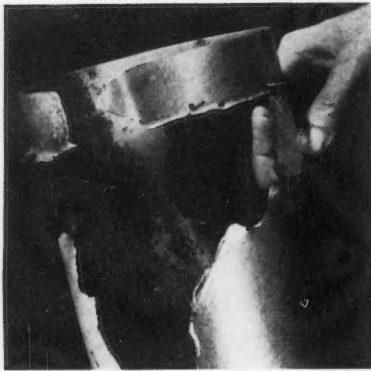
Figure 11—General corrosion of Type 316 downcomer in 40 percent acetic acid contaminated with 1.5 percent formic acid at 240 F.
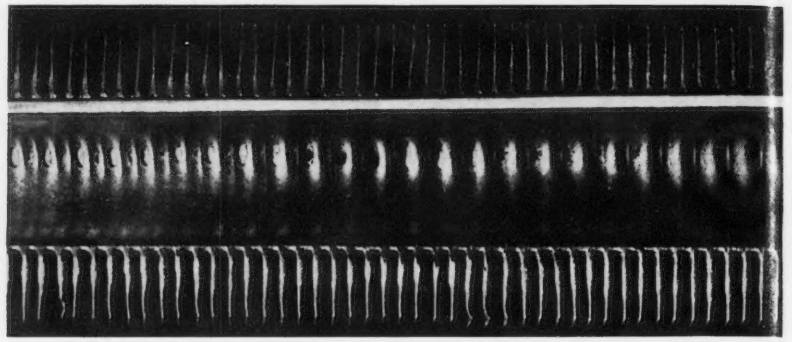
Figure 12—Effect of temperature on the corrosion of a Type 316 finned tube.

ASTM standards for quality and composition. Fabrication techniques should be such that these materials are not exposed to sensitizing temperatures 800 F-1500 F for excessive periods. Surface cleanliness and freedom from iron contamination should be insisted upon.

3. Molybdenum Containing Austenitic Stainless Steels. AISI Type 316, 317 and 318 Stainless Steels

AISI Type 316 stainless steel is the principal material of construction used for chemical production equipment in acetic acid service. It has a wide range of passivity to the conditions of temperature, acid concentration, organic and inorganic contaminants normally encountered in the production of acetic acid. It is adequately resistant to all concentrations of pure acid up to their normal boiling point and can tolerate larger amounts or organic and inorganic contaminants that can be the non-molybdenum containing grades of stainless steel.

A large number of special analysis specifications within the ASTM allowable range for Type 316 are in common use by many companies for acetic acid service.

These specifications call for higher chromium and molybdenum minimum contents and lower maximum carbon contents. A typical analysis is shown in Table 10.

At one time the belief was widespread that such special requirements on the chromium, molybdenum and carbon contents were required for all acetic acid services. Data from isolated locations, such as in Table 11, could be produced to support this contention.

More recent and comprehensive tests in process streams as several acetic acid producing plants indicate that stainless steel analysis within the current ASTM and AISI limits are satisfactory for the majority of acetic acid services. Only in isolated cases, notably in the presence of reducing contaminants such as formic acid and dilute sulfuric acid, are modifications of these analyses justified. Figure 10 illustrates the general trend of the effects of nickel, chromium, molybdenum and carbon on the corrosion resistance of Type 316 stainless steel in an acetic acid environment. Even under this reducing environment where analysis variations are likely to be most important, the variation has little practical significance. In some iso-

lated cases higher chromium and molybdenum may be detrimental.

The presence of small amounts of ferrite, due to composition unbalance, seems to have very little effect on the corrosion resistance of Type 316 stainless steel in acetic acid service and some two phase alloys have been used industrially.

Type 318, (Columbium stabilized Type 316) has found limited use where intergranular corrosion of Type 316 stainless steel is a problem. The extra low carbon grades of Type 316 provide similar resistance to intergranular attack.

Type 317 stainless steel is used occasionally in acetic acid plants where the oxidizing capacity of the process stream is insufficient to maintain passivity of Type 316 stainless steel.

4. 25% Chromium—12-20% Nickel AISI Types 309, 310 and 314 Stainless Steels

These alloys are used to a limited extent in acetic acid services where their superior elevated temperature physical properties are required. The addition of molybdenum to these alloys improves their corrosion resistance to liquid acetic acid streams.

5. 25-30% Chromium—3-5% Nickel AISI Type 329 Stainless Steel

This alloy, which has been very popular in European industry, is receiving increased attention in this country. Type 329 has excellent resistance to boiling acetic acid solutions below 50 percent concentrations as indicated in Table 13, and increased resistance to reducing impurities in these dilute acid streams.

Table 14 shows the result of a field corrosion test in an operating 316 stainless steel thermosyphon type reboiler which required major repairs at 6-month

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TABLE 10—Typical Special Analysis for Type 316 Used in Acetic Acid Service

ELEMENT	ASTM A240 Grade M, Percent	Company Standards, Percent
Carbon, max.	0.08	0.06
Manganese, max.	2.50	2.50
Phosphorous, max.	0.035	0.035
Sulphur, max.	0.030	0.030
Silicon, max.	0.85	0.85
Chromium, min.	17.00	17.50
Nickel, min.	10.00	10.00
Molybdenum, min.	2.00	2.50

TABLE 11—Field Corrosion Test: Effect of Composition on Corrosion Resistance of Stainless Steel in Condensate From Boiling 80% Acetic Acid, 210 F, 500 Hr.

ANALYSIS*				Corrosion Rate, IPY
% MO	% CR	% NI	% C	
....	18.04	9.69	0.08	0.04000
1.29	18.25	12.09	0.08	0.0096
1.72	18.04	13.73	0.06	0.0081
2.67	16.75	12.35	0.08	0.0026
2.18	18.02	13.75	0.07	0.0014
3.30	17.92	13.61	0.08	0.0002

* All specimens heated to 1100—1150 F for 15 minutes and air cooled.

TABLE 12—Field Corrosion Test: Boiling 99.9 + % Acetic Acid (High Assay) 360 Hours

MATERIAL	Corrosion Rate, IPY
Type 316	0.0035
Type 317	0.0021
Type 329	0.0022
Type 410	0.5850
Type 430	0.2690
"20" Alloy	0.0027
Admiralty	0.0024
Nickel	0.0024
Nionel	0.0017
Hastelloy C	0.0001
Titanium	0.0001

TABLE 13—Laboratory Corrosion Test: Corrosion of Type 329 S.S. in Boiling Acetic Acid Solutions

%, Acetic Acid	Corrosion Rate, IPY
2	0.000
30	0.000
40	0.000
50	0.000
70	0.119
100	0.145
100*	0.002
100**	0.005

* 316 S.S. Annealed, included for comparison
** 316 S.S. sensitized, included for comparison

TABLE 14—Field Corrosion Test: 12% Acetic Acid Containing 0.5% Formic Acid, 280 F, 4000 Hr. Reboiler Under Moderate Pressure

MATERIAL	Corrosion Rate, IPY
Type 316	0.0137
Type 329	0.0001
Type 310	0.0033
"20" Alloy	0.0088
Hastelloy B	0.0087
Nickel	0.1*
85/15 Red brass	0.0417
70/30 Cu — Ni	0.0259
3% silicon bronze	0.0202
Admiralty	0.0228

* Specimen destroyed.
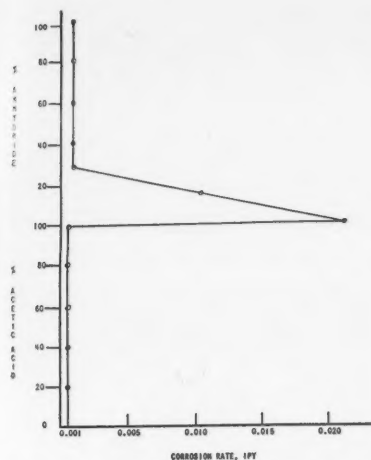
Figure 13—Laboratory test of corrosion by acetic acid, acetic acid-acetic anhydride mixtures on Type 316 stainless steel.
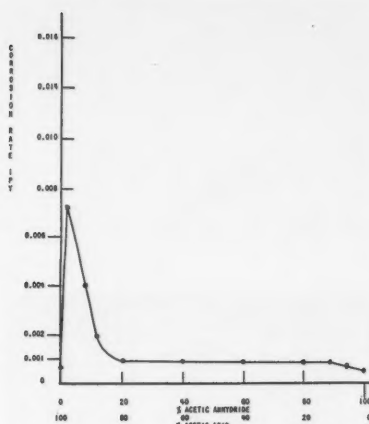
Figure 14—Field test corrosion of acetic acid-acetic anhydride mixtures on Type 316, boiling, sieve tray column.

Figure 15—Pitting attack of Type 304 tower shell caused by striking welding arc on shell and weld flux spatter.

intervals. The tube bundle and tube sheet were replaced with type 329 stainless steel and no corrosion has been noted on these materials in the three years since the substitution. Unfortunately, Type 329 is not readily available in plate and sheet form and its use to date has been limited to tubing, forgings and castings.

6. 20% Chromium—29% Nickel, Copper Molybdenum, Stainless Steels "20" Class Alloys, Worthite.

These alloys find limited use in the acetic acid industry, particularly as valves and pumps, under reducing conditions which limit the successful use of Type 316 stainless steel, such as acetic acid solutions contaminated by dilute sulfuric acid. While not completely explored, it seems possible that the "20" type alloys may have greatly superior resistance to stress corrosion cracking in acetic acid environments contaminated by small amounts of organic chlorides.

Common Corrosion Problems

1. General Attack

While Type 316 stainless steel has a wide latitude of resistance to most acetic acid concentrations at temperatures through their normal boiling points, the presence of some contaminants, particularly formic acid, sulfuric acid and hydrochloric acid, can cause rapid general attack on stainless steel. Such attack is illustrated in Figure 11. Where possible, these contaminants should be eliminated or their concentration reduced by dilution. In some cases where the inorganic acids are present as catalysts, substitution of oxidizing acids, such as phosphoric acid, is beneficial.

Temperature reduction of the process streams often is an effective control measure to bring general corrosion down to an acceptable level. Figure 12 illustrates the important effect of temperature on a Type 316 stainless steel finned tube. At areas where the fins have conducted heat away from the tube wall, attack has been light compared to the complete penetration between fins.

Inhibition of general attack by the introduction of oxidizing agents, such as permanganate, dichromate, cupric and ferric salts, or air injection, is sometimes effective. Table 15 illustrates the effec-

tive injection of 200 cubic feet of air per hour to the base of an operating acetic acid column for corrosion control of Type 316 stainless steel.

Extreme caution must be used in applying oxidizing inhibitors. Pitting and oxygen concentration cell (crevice) attack of stainless may result from use of insufficient inhibitor to completely passivate the crevices as well as the surface. Any copper equipment in the system will be subject to increased rates of corrosive attack. The combination of strong oxidizing agents (sodium dichromate or potassium permanganate), high assay acetic acid (99.9 percent), boiling temperatures and high velocity are particularly corrosive to Type 316 or other austenitic stainless steels with rates approaching 0.5 ipy being reported.

The presence of 0.3 to 5% acetic anhydride in glacial acetic acid can result in severe general corrosion of stainless steels, particularly at boiling temperatures. Figures 13 and 14 illustrate this peak in the acetic acid—acetic anhydride corrosion curve.

Frequent plant failures occur because of the substitution of Type 304 stainless steel for Type 316 stainless steel in high temperature, acetic acid processing equipment. It is not uncommon for mixups in these materials to occur at the suppliers' warehouses, during manufac-

ture or fabrication, in plant warehousing, etc. This results in premature failure of equipment due to corrosion of the 304 stainless steel material.

To avoid such costly errors, some plants chose to stock and use only Type 316 stainless steel even though the less expensive Type 304 stainless steel might have limited use in the plant. In other plants where economics dictate the use of both materials, spot tests for molybdenum are run on all incoming stainless steel plate, sheet, tube, parts, etc., even such parts are plainly marked as Type 316 stainless steel. Similar spot testing for molybdenum on all line sections, tower sections, valves, pumps, after fabrication of acetic acid units may prevent costly future unit shutdowns after production is underway.

2. Pitting Attack

Austenitic stainless steels are subject to pitting type of attack in some acetic acid solutions. Such attack is most common when the acid is contaminated by inorganic chlorides or inorganic acids such as hydrochloric or sulfuric. Pitting attack is most frequently associated with discontinuities of the metal surface such as slag or steel inclusions or under deposits of foreign matter. Stainless steel

TABLE 15—Field Corrosion Test: Inhibition of Stainless Steel Corrosion by Air Injection. Rates Before and After 200 Cubic Feet Per Hour, Air Injection Into Base of Operating Distillation Column.

CONDITIONS	LOCATION		
	Top	Middle	Base
Temperature	210° F	230° F	250° F
Acetic acid	24%	40%	88%
Formic acid	1%	1.5%	2%
Propionic acid			4%
Butyric acid			2%
Water	75%	58.5%	4%
MATERIAL	Corrosion Rate, IPY Before Air Injection (Average of 5 Test Racks per Location) 5000 Hrs.		
Type 304 S.S.	0.051	Specimens destroyed	0.013
Type 316 S.S.	0.006	0.009	0.003
Admiralty	0.002	0.007	0.001
MATERIAL	Corrosion Rate, IPY After Air Injection, 1000 Hrs.		
Type 304 S.S.	0.0001	0.045	0.0150
Type 316 S.S.	0.0003	0.0002	0.0002
Admiralty	0.040	0.009	0.002
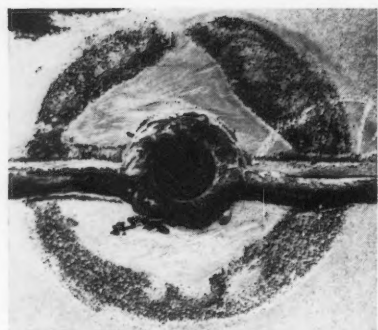
Figure 16—Intergranular attack of Type 316 in heat affected zone of poor nozzle weld.
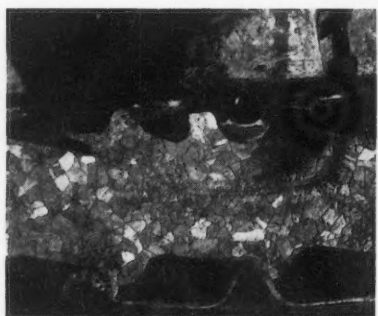
Figure 17—Intergranular attack and excessive grain size on Type 316 cast atmospheric condenser head.

Figure 18—Intergranular attack around acicular grains of Type 316 casting resulted in flexibility.

Figure 19—Crevice corrosion of Type 316 bolting under nuts in acetic acid.

Figure 20—Crevice corrosion of Type 316 tray support.

Figure 21—Gasket surface corrosion of Type 316 flange.

intended for acetic acid service should have reasonably smooth, annealed and cleaned surfaces. An ASTM A-240, No. 1 finish is commonly specified. The use of more highly polished finishes is seldom justifiable. Surface cleanliness should be maintained during every phase of stocking, handling, fabrication, erection and testing of stainless steel for acetic acid service.

Pitting attack of stainless steel in acetic acid solutions is known to have resulted from:

a. Impression of iron particles into the surface by workers walking over sheets prior to fabrication or by handling with rusty steel tools.

b. Iron contamination from grinding wheels, steel wire brushes, and steel chipping hammers.

c. Incomplete removal of weld flux and weld metal splatter.

d. Tack welding and position lug welding with carbon steel without complete removal of the steel prior to exposure.

e. Slag inclusions or porosity in welds.

f. Striking welding arc on the sheet or plate surface instead of in the immediate weld area.

g. Pickling after fabrication in spent and dirty muriatic acid baths previously used for carbon steel.

h. Painting or marking inside of vessel with oil base paint or crayon.

Bar stock items, including bolting, tie rods, valve discs, etc., are susceptible to a type of pitting attack commonly referred to as "honeycomb" attack. This pitting results from the alignment of carbides, slag-inclusions and other impurities in the direction of drawing, leaving long, almost continuous paths of inferior corrosion resistance. This type

of attack can be eliminated by the use of properly quenched annealed material.

Figure 15 shows pitting attack of Type 304 stainless steel due to weld and weld flux splatter and careless striking of a welding arc.

Pitting attack is controlled largely by: Elimination or reduction of the halogen ion or mineral acid responsible for the attack, lowering the operating temperature, proper surface cleaning before exposure, or addition of passivators. As pitting is frequently the result of oxygen concentration cells, either increasing the degree of aeration or eliminating it altogether is an effective control measure. Cleanliness during fabrication and routine removal of all foreign deposits formed during operation can prevent many cases of pitting from developing.

The molybdenum containing grades of stainless steel have superior resistance to pitting type of attack and should be used in those acetic acid applications where susceptibility to such attack is expected.

3. Intergranular Attack

The phenomenon of intergranular attack of the austenitic stainless steels, particularly in the heat affected zones of welds, has been thoroughly covered in existing technical literature. While this form of attack does not constitute a major problem to the acetic acid industry, sufficient cases of such attack have occurred to deserve mention.

Relatively pure acetic acid solutions do not cause intergranular attack on the commonly used Type 304 and Type 316 stainless steel meeting ASTM quality standard with regard to carbon content and when these materials are in the annealed condition, fabricated by welding techniques designed to minimize heat input into the parent metal. Post fabrication heat treatment, rapid quench methods during welding, the use of stabilized materials, or the use of extra low carbon steels are not required for general acetic acid service.

However, the use of high carbon steels (over 0.08 percent C) in the unannealed

condition with excessive heat input during fabrication will leave the stainless steel susceptible to such attack. Contamination of the acid to give reducing or highly oxidizing environments can result in intergranular attack. Where these conditions prevail, the use of the extra low carbon grades of stainless is generally preferred to the use of stabilized materials.

Figure 16 illustrates the importance of good welding technique in maintaining resistance to intergranular attack. In this example, areas adjacent to good weld seams are unaffected while areas adjacent to excessive weld metal deposited in a manner to give high heat input into the parent metal are severely attacked.

Intergranular attack of stainless steel castings is illustrated in Figure 17. This 316 stainless steel atmospheric condenser head shows the excessive grain growth common to large stainless castings and carbide precipitation around the grain boundaries. Exposure in acetic acid without proper annealing resulted in intergranular attack around the large grains ($\frac{1}{2}$ inch to $1\frac{1}{2}$-inch diameter) and subsequent leakage.

Figure 18 shows another unusual case of intergranular attack on a baffle from a similar cast condenser head. During cooling, the metal solidified from both sides of the mold in acicular or needle like crystals with carbide precipitation around every crystal. Subsequent intergranular attack in acetic acid left these crystals intermeshed and the baffle intact but as flexible as ordinary rope.

4. Crevice Corrosion

Crevice, contact, oxygen concentration cell, or metal ion concentration cell attack is common in acetic acid solutions. Such attack is the result of part of the stainless surface being shielded from other areas of the steel either by contact or deposits. When the environment
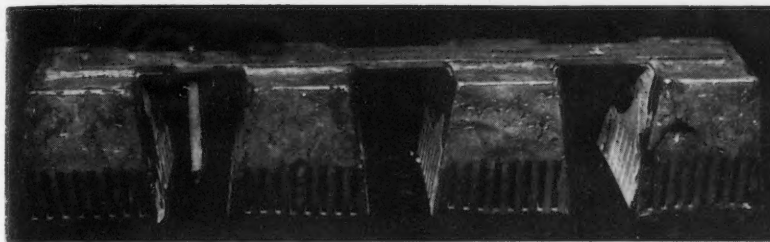
Figure 22—Stress corrosion cracking of Type 316 bubble caps.

Figure 23—Dilute acid storage in wooden tanks.

Figure 24—Corrosion of steel bands on wooden tanks storing acetic acid.

is such as to allow potential differences to exist between the shielded area and unshielded area and the ratio of the shielded area to unshielded area is low, this type of attack may be severe. Figures 19 and 20 are examples of crevice corrosion of stainless steel.

Crevice corrosion is controlled largely by proper design to minimize crevices and by control of velocities to insure adequate flow of media to all surfaces. Welded joints are preferred to screwed connections and butt joints are superior to lap joints for acetic acid service. Full penetration welds and cleaning of all weld metal, weld flux splatter, or other deposits will minimize the possibility of such attack. Elimination of air leakage and pressurizing to minimize air leakage are frequently effective control measures.

Gasket surface corrosion of stainless steel is a specialized form of crevice corrosion common in acetic acid service (Figure 21). Such attack is believed to be due to the wicklike action of asbestos gaskets which holds part of the process stream in stagnant contact with the gasket surface. Impurities in the gasket material, particularly chlorides and sulfates, or lack of aeration in these areas, result in the formation of anodic areas subject to crevice corrosion.

Gasket surface corrosion can be minimized by the use of well washed asbestos gaskets whose bonding agent is such as to minimize the wick effect or by the use of impervious gasket surfaces. The use of impervious gasket surfaces, Teflon and Neoprene, minimizes attack under the gasket but does not eliminate attack around the edges.

5. Stress Corrosion Cracking

Either organic or inorganic chloride contamination of acetic acid solutions can result in stress corrosion cracking of the austenitic stainless steels. The severity of such attack increases as the temperatures approach the boiling point and frequently is more severe in vapor areas than in liquid areas. Figure 22 shows stress corrosion cracked bubble caps.

Unfortunately this type of attack, which is one of the major causes of failure of austenitic stainless steels, has not been as completely explored as the other forms of corrosion. On the basis of present knowledge, the positive approach to elimination of stress corrosion cracking problems is by elimination or dilution of the source of chlorides, reduction in temperature, or by substitution of materials resistant to stress corrosion cracking.

External corrosion of stainless steel acetic acid equipment by stress corrosion cracking is common also. The two most frequent causes of such attack are the use of improperly washed insulation

without complete surface sealing and improper design of heat exchangers to allow splash areas to exist on the water side of tubes. In the first case, moisture penetrates the insulation, leaching out chlorides and carrying them down to the hotter pipe, tank or vessel surface. The moisture is partially evaporated at these surfaces, allowing chloride levels to build up to the stress corrosion cracking level on the stainless surface. In the second case, tubes not completely and continuously washed by the cooling water also will evaporate moisture in the splash areas causing concentration of chlorides to the stress corrosion cracking level.

Other Materials

Metals

1. Steel, Cast Iron, High Silicon Cast Iron

Steel and cast iron exhibit very high corrosion rates at boiling temperatures in acetic acid solutions at all concentrations. In acid concentrations below 50 percent at room temperature, these materials may be considered if the relatively high corrosion rates and iron pickup can be tolerated. Typical rates for iron and steel are given in Table 16.

The high silicon cast irons such as Duriron are resistant to most acetic acid solutions in all concentrations at temperatures through boiling. These materials are occasionally used for pumps and other cast equipment in acetic acid service.

2. Monel, Inconel and Nickel

The nickel alloys find only limited use in the acetic acid industry under conditions where aeration, acid concentration and temperatures are low. Monel generally is chosen for unaerated services. Its corrosion rate reaches a peak at about 50 percent acid concentration and decreases to about 0.008 ipy in glacial acetic acid. The usefulness of this alloy is destroyed by environmental conditions which are highly aerated or include strong oxidizing agents. Inconel has superior tolerance to oxidizing conditions, but its use is limited to dilute acid concentrations at elevated temperature.

3. Hastelloy B, C and D

The various Hastelloy alloys are resistant to pure acetic acid solutions at all normal concentrations and temperatures. These materials are sometimes used in the acetic acid industry where the acid is used in conjunction with inorganic acids and salts which limit the successful use of stainless steel or the copper alloys. Alloys B and D are used under reducing conditions such as with combinations of acetic acid and dilute

sulphuric acid. Alloy C is most commonly used in acetic acid solutions which are highly oxidizing in nature such as with copper sulfate, chromic acid, dichromates and permanganates.

4. Silver and Lead

Silver has been used frequently in European practice to handle all concentrations and temperatures of acetic acid solutions. Very little use has been made of silver, silver clad or silver plated equipment in the American acetic acid industry. Silver condenser tubes have been in use in one domestic plant for 99.7 percent acid and anhydride for nine years.

Lead has only limited resistance to acetic acid solutions. It has been used principally in glacial acetic acid storage and handling where temperatures, degree or aeration and velocities were low. Dilute acetic acid solutions, even at room temperature, attack lead at rates exceeding 0.050 ipy. These rates increase rapidly as aeration and velocity increase.

5. Titanium, Tantalum and Zirconium

These alloys are unaffected by pure acetic acid solutions at all normal concentrations and temperatures and may find limited use in the acetic acid industry for specialized equipment in the handling of mixtures of acetic acid and inorganic acids such as hydrochloric acid.

TABLE 16—Laboratory Corrosion Test: Corrosion Of Steel And Cast Iron In Acetic Acid Solutions, 1 To 48 Hours

MATERIAL	% HAc	Temperature °F	Corrosion Rate IPY
Nodular cast iron.	5	210	12.000
Gray cast iron....	5	210	9.500
Mild steel........	5	210	2.250
Nodular cast iron.	100	95	0.053
Gray cast iron....	100	95	0.080
Mild steel........	100	95	0.067
Mild steel........	99.8	Room	0.030
Mild steel........	95.5	Room	0.040
Mild steel........	49.7	Room	0.008
Mild steel........	20.5	Room	0.008

Non Metallic Materials

1. Glass, Glass Lining and Chemical Stoneware

Glass lined tanks, glass piping and chemical stoneware equipment are frequently used for the storage and handling of pharmaceutical grades of acetic acid and for industrial combinations of acetic acid and other corrosive chemicals which rapidly attack the more common alloys.

2. Plastics

Washed asbestos or carbon filled, phenol formaldehyde, bonded plastics such as Haveg and Karbate 22 are successfully used in acetic acid processing equipment where metallic materials may not be satisfactory.

Limited use has been made of both polyethylene and unplasticized polyvinyl chloride in pure acetic acid solutions at lower temperatures. Laboratory data indicate that at 40 C acetic acid is specific for the stress cracking of polyethylene. Contamination of acetic acid solutions by other organic compounds, ketones, esters, etc. may materially reduce the life of these plastics in acetic acid service.

3. Rubber

Rubbers, either hard or semi-hard, have been successfully used for the lining of acetic acid storage tanks and for hose applications.

Natural rubbers and neoprene are satisfactory in all acid concentrations up to a temperature of 120 F, when the color pickup from rubber is not objectionable.

4. Wood

Wood stave storage tanks have been used extensively for the storage of dilute acetic acid. While modern design calls for the use of austenitic stainless steels, hundreds of wooden tanks are still in service after 10 to 30 years' use, (Figure 23). Such tanks are subject to acid seepage through the wood with subsequent acid loss and corrosion of the steel bands or concrete foundations, (Figure 24). Various microwaxes and linings have been tried to limit this seepage with limited success only.

C. Coatings

Under conditions of atmospheric contamination or occasional splash or spill coatings of the following types have been successfully used: Catalyst cured modified phenolics, air dry phenolics, polyvinyl chlorides, vinylidene chloride copolymers, epoxy resins and synthetic or natural base rubber paints. No coatings are completely satisfactory for constant immersion in acetic acid although coatings of the baked phenolic type show the most promise.

Current Requirement for Cathodic Protection Of Oil Well Casing*

By E. W. HAYCOCK

Introduction

DURING THE past decade, external corrosion of oil well casing has become recognized as a problem of increasing economic importance. Battle,[1] in 1953, reviewed the casing corrosion problem and discussed the economics involved, the possible causes of corrosion, and the suggested methods of reducing the attack. Since that time, cathodic protection has emerged as the most attractive method of combating casing corrosion for both new and existing wells. This choice is based to a large extent upon the conviction that, regardless of the specific mechanism, the corrosion involves electrochemical reactions and therefore can be completely suppressed if sufficient cathodic protection current is applied. This conviction arises from confidence in an understanding of the principles of cathodic protection which has been gained from numerous examples of its successful application to similar corrosion systems.

Several investigations of the problems involved in applying cathodic protection to oil well casing have been reported in the literature.[2-9] Most of the investigations reported have been concerned with the protection of relatively shallow wells of depths up to 5000 feet. Sudbury, Landers, and Shock[6] have included measurements on deeper wells, and recently Ballou and Schremp[8] have described tests with wells requiring protection to depths greater than 8000 feet. Three principal questions which arise in the application of cathodic protection to oil well casing are:

(a) Can sufficient current be distributed economically to the lower depths of the casing requiring protection?

(b) Will the application of cathodic protection produce secondary deleterious effects?

(c) How much current is required to give complete protection in any given circumstance?

The uncertainties involved in answering these questions become greater for deeper wells.

Distribution of applied current in oil well casing has been studied by potential profile measurements[(1)] and, in general, this method has been found to be satisfactory. Adverse effects of cathodic protection, such as electrolytic corrosion produced at the base of the surface string and stray current corrosion, have been considered by Sudbury, Landers, and Shock[6] and by Barrett and Gould.[4] Although the oc-

E. W. HAYCOCK has been a chemist in the Materials Engineering and Corrosion Department of the Emeryville Research Center of Shell Development Company since 1953. He obtained a BSc. degree in 1948 and a PhD degree in 1951 from the University of Bristol, England, working in the field of chemical reactions of the solid state under the supervision of Professor W. E. Garner, F.R.S. Prior to joining Shell he worked for two years on problems involving the structure of liquids as a Research Associate of Professor Joel H. Hildebrand at the University of California at Berkeley.

Abstract

Methods at present used to indicate the minimum applied current required to give complete cathodic protection are discussed and evaluated in terms of their scientific basis and their applicability to the protection of oil well casing .Laboratory experiments are described involving the application of cathodic protection currents to a series assembly of galvanic cells. The results of these experiments lead to a modification of the log current—potential criterion of complete protection widely used at the present time. The experiments also indicate the amount of corrosion repressed as a function of the applied protection current, information which is of considerable value when an economic balance is involved.

5.2.4

currence of these effects would be of serious concern, they can be counteracted if they are found to exist. Theoretical and experimental studies of current distribution and possible adverse effects of cathodic protection have been made by Eldredge.[10] His conclusions concerning possible adverse effects are essentially in accord with those of Barrett and Gould.

The question of the amount of current required to achieve complete protection is one which has attracted a great deal of attention, and several criteria have been suggested whereby this current can be determined. The purpose of this paper is to review these criteria of protection and to describe experimental studies which suggest a modification of the widely used log current—potential break criterion. The experiments reported here were part of a cooperative laboratory and field investigation carried out in conjunction with Shell Oil Company, Pacific Coast Area, Coastal Division. The problems involved were concerned with the application of cathodic protection to the relatively deep wells (to 11,000 feet) existing in the Ventura Avenue Field, Ventura, Cali-

Figure 1—Schematic polarization diagram for cathodic protection of a single corrosion cell.

fornia. The field experiments are not described here but will be dealt with in a future paper from the operating group. The experiments described are of a general nature, and the results reported should be useful in applications other than the protection of oil well casing (e.g., buried pipe lines).

Criteria of Current Requirements for Complete Protection

For clarity in discussing the scientific basis of several of the current requirement criteria, it is beneficial to refer to the schematic polarization diagram shown in Figure 1 for a single corrosion cell. Similar diagrams have been described by Mears and Brown[11] in their early work on the theory of cathodic protection. The potential of each electrode is shown as a function of the electrode current. Lines AB and CBD are the anode and cathode polarization curves, respectively, the point A representing the open circuit potential of the anode and C, the open circuit potential of the cathode. The lines intersect at the point B which, neglecting the internal cell resistance, defines the natural corrosion potential and corrosion current (I_c) of the cell.

The accepted theory of cathodic protection requires that when an external current, I_E, is applied to the system, the cathode potential moves along BD to F, and the anode potential along BA to E. As the protection current is increased, E approaches A and F approaches D. The theory states that when E reaches A (i.e., when the polarized corrosion potential B' is equal to the open circuit anode potential), then the anode current is zero and, hence, no corrosion is occurring. The point D, therefore, defines the external current required for complete protection, I_p. In practice, I_p cannot be measured directly. Several criteria have been proposed for determining it by indirect methods.

The criteria of current requirements for complete protection which have been considered for application to oil well casing are itemized below. The first four of these criteria can be illustrated by direct reference to Figure 1.

Criterion (1)

With Criterion 1, sufficient current is required to give a polarization potential of the structure, in addi-

tion to any IR drop, of —0.85 volt with reference to a copper-copper sulfate electrode.

Referring to Figure 1, this criterion assumes that the open circuit anode potential, A, will not be more than 0.85 volt above the Cu-CuSO$_4$ reference electrode. The magnitude of the critical polarization potential widely accepted (i.e., —0.85 volt) is based mainly upon experience in protection of pipe lines. If this criterion is to be used for oil well casing, the potential at the bottom of the casing has to be measured or estimated in some way. Ballou and Schremp[8] suggest a formula by which the "bottom hole" potential can be estimated from the potential measured at the wellhead.

The use of this criterion for pipe lines has been criticized by Ewing[12] and Logan[13] on the basis that it is uncertain in which direction the potential will shift after protection currents have been applied for some time. It is not certain that this objection is valid in oil well casing application. The principal objection appears to be that the choice of —0.85 volt may not be an accurate estimate of the potential corresponding to complete protection.

The open circuit anode potential of steel depends upon the activity of ferrous ions in the environment. For pure iron, the reversible electrode potential as a function of the ferrous ion activity is given by the Nernst equation.[14]

$$E = -0.441 \text{ volt} + 0.0295 \log [Fe^{++}]$$

referred to the hydrogen electrode. Using this equation and the solubility product relationship $[Fe^{++}][OH^-]^2 = 10^{-14.65}$, it can be shown that an iron potential of —0.85 volt, referred to a Cu-CuSO$_4$ electrode, corresponds to the ferrous ion activity in equilibrium with ferrous hydroxide in aqueous media at pH of 8.28. Therefore, if pure iron is maintained at a potential of —0.85 volt (Cu-CuSO$_4$) in equilibrium with Fe(OH)$_2$ at a pH = 8.28, no corrosion will occur. In practice, the correspondence of —0.85 volt to complete protection depends upon the deviation of the practical conditions from those used in the above calculation. These deviations could be large.

Experience has shown that —0.85 volt is generally a conservative value for practical use with pipe lines. The economic consequences of underestimating the current requirements for complete protection are discussed in a later section. In oil well casing application, due to the relatively large protection currents required, an overestimation could lead to significant unnecessary expenditures.

Criterion (2)

With this criterion sufficient current is required to raise the potential of the corroding structure 0.2 to 0.3 volt above its average corrosion potential.

This is similar in many respects to criterion (1). However, it depends upon the assumption, based on experience, that the average corrosion potential of steel in soils will not lie more than 0.2 to 0.3 volt below the open circuit potential of the anodic areas (i.e., referring to Figure 1, B is not more than 0.3

Figure 2—Schematic diagram of apparatus for study of steel versus platinum corrosion cell.

Figure 3—Polarization potentials versus electrode current for steel-platinum corrosion cell.

Figure 4—Polarization potentials versus applied protection current for steel-platinum corrosion cell.

volt less than A). This implies that the corrosion is mainly under cathodic control, which is generally true for steel structures in underground environments. This criterion has the same indefinite features as those described for criterion (1).

Criterion (3)

With this criterion sufficient current is required to give a break (i.e., a sharp discontinuity) in the applied current vs structure potential relationship or, more commonly, a break in the plot of log current vs potential.

This is probably becoming the most widely used criterion in oil well casing applications. As a general criterion, it has its origin in the work of Evans, Bannister, and Britton[15] and has been discussed in detail by numerous authors, notably Ewing,[12] Logan,[13] Pearson,[16] and Mears.[17] When a protective current is applied to a corroding structure, the anode and cathode polarization potentials are not identical functions of the applied current. When the current is reached at which the corroding structure achieves complete protection, the total structure surface begins to follow a cathodic polarization curve and a break is observed in the current vs potential plot. At current densities sufficient to evolve hydrogen from the total surface, the current-potential relationship becomes a hydrogen overvoltage curve and is found to obey the Tafel equation[12] (i.e., the log current vs potential plot becomes a straight line). Mears[17] showed this criterion to be of general validity in corrosion systems where only slight anode polarization occurs. However, he states that in numerous laboratory tests, the limiting current density required for complete protection was greater than that indicated by the potential break method.

The main difficulty in using this criterion lies in the choice of the exact position of the break in the curve. In most applications the log current vs potential plots do not show a sharp break but take the form of two essentially straight lines joined by a curved section over the region of the break. It has become customary to select the break point as the intersection of the two straight line portions of the curve, extrapolating these lines to an intersection if necessary. A modification of this criterion is suggested as a result of the experiments described in a later section of this paper.

Criterion (4)

A specified average current density is required for complete protection when this criterion is used.

In cases where there is only slight anode polarization, the current required for protection will be somewhat greater than, but approximately equal to, the corrosion current. Therefore, from metal loss rate data, it is possible to estimate the protective current required for these particular circumstances. It will be seen from Figure 1 that, when the anode polarization is slight, B approaches D and I_c approaches I_p. In pipe line practice it is found that a range of current densities are required under various soil conditions. The criterion can be used, at best, as a secondary estimate of current requirement. It is especially unsatisfactory in applications where the corrosion rates and distribution of corrosion are not known.

Criterion (5)

Sufficient current is required to suppress the appearance of the anodic portion of the potential profile curve.

This criterion has been studied extensively.[2,4,6,8] Potential profile curves are valuable for indirect surveys of external casing corrosion and for current distribution studies. Since they involve measuring potential differences between points 25 feet apart on the casing (with tools presently available), they do not detect currents flowing between localized anodes and cathodes. Moreover, the appearance of recovered casing from Ventura and other fields indicates that local cells could exist circumferentially around the casing. In these cases potential profile measurements, which detect only the vertical components of currents flowing in the casing, are inclined to give low estimates of the current required for complete protection.

Criterion (6)

With criterion 6, sufficient current is required to change the environment chemically by an arbitrary amount (e.g., to produce a certain amount of alkalinity).

This criterion has been suggested for special applications and may be useful in cases where sulfate reducing bacteria are known to be the principal corrosive. Attaining a chosen pH would be effectively
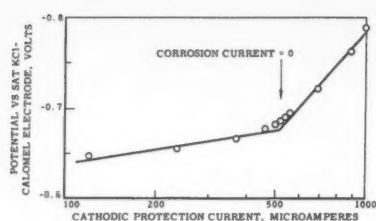
Figure 5—Average polarization potential versus log applied current for steel-platinum corrosion cell.
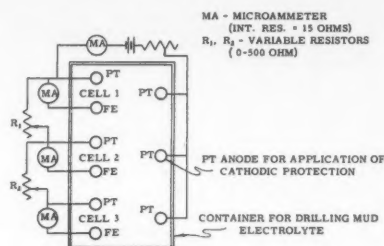
Figure 6—Circuit plan for laboratory studies of cathodic protection with multiple cell apparatus.
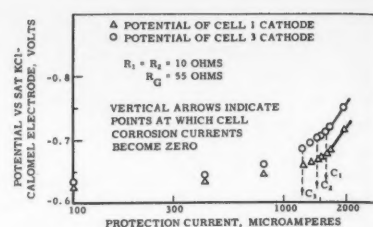
Figure 7—"Shallow well" model cathodic protection log current-potential curve.

applying a bactericide. It appears that this criterion cannot be made definite enough in its execution to allow it to become one of general application.

Reviewing the six criteria discussed, it becomes apparent that only (1), (2), and (3) may be considered primary methods for determining the limiting current required for protection. Criteria (4) and (5) can be used as secondary indications. It should be pointed out that the data required to apply criterion (5) are relatively expensive to obtain. Criteria (1) and (2) are based on experience obtained principally from pipe line protection. In a relatively new application, such as oil well casing protection, little or no experience is available. There is a degree of uncertainty involved in assuming that steel exposed to deep subterranean formations will display the same open circuit anode potentials as it does in surface soils. The requirements of criterion (3), on the other hand, are basically definite and do not depend directly upon the environment. Neither the open circuit anode potential nor the average corrosion potential are of direct concern. The limitations on the use of criterion (3) are that the corrosion system must be under cathodic control and the break in the log current vs potential curve, corresponding to complete protection, must be determinable with a fair degree of accuracy.

To explore this latter point in more detail, laboratory experiments have been made in which cathodic currents have been applied to a connected set of galvanic corrosion cells arranged to simulate a corroding casing string.

Experimental Procedures and Results

Initial experiments were made with a single steel-platinum galvanic couple immersed in a Ventura drilling mud gel. These experiments were designed to measure the polarization potentials of the individual electrodes as a function of the applied current and to check the log current vs potential break criterion for this simple system.

The apparatus employed is shown schematically in Figure 2. The corrosion rate of the steel anode could be followed by measuring the current flowing between the steel and platinum electrodes. The potentials of both the anode and the cathode could be measured at any time with respect to saturated KCl calomel electrodes. The calomel electrodes were

connected through salt-agar bridges to 1 mm diameter tubular probes placed as shown in the diagram with their ends one tube diameter from the electrodes. Potential measurements were made with the current flowing and hence contain a corresponding IR term. This should be small due to the proximity of the probes to the electrodes. The last inch of each probe was filled with drilling mud gel to obviate possible disturbances due to salt diffusion from the bridges to the electrode surfaces. An additional platinum electrode was immersed in the electrolyte and placed in the circuit so that various controlled protection currents could be applied to the corrosion cell.

For the experiments with single corrosion cells and for those described later with a multiple cell assembly, the drilling mud electrolyte was a high pH, lime base mud with the pH reduced to 7.5 by treatment with CO_2. The specific conductance of this mud, when allowed to gel, was approximately 2.7×10^{-3} mhos. The use of drilling mud as an electrolyte enabled the corrosion cells to be studied under anode polarization conditions similar to those experienced by oil well casing.

It was found that platinum wire or foil, wrapped with glass wool, gave a stable cathode which showed very little permanent polarization effect from the periodic application of cathodic protection currents. The glass wool wrapping improved the availability of oxygen depolarizer at the cathode surface and hence maintained a higher rate of corrosion. A cell consisting of a $\frac{1}{4}$ inch x 1 inch carbon steel anode placed two inches from a glass wool wrapped platinum cathode (4 inches of 50 mil wire or $\frac{1}{2}$ inch x 2 inch x 20 mil foil) gave a stable yet vigorous steel corrosion rate when the atmosphere over the cell was air. The internal resistance of these cells was in the range 40-50 ohms. Steady state conditions were achieved in two to three days.

In the absence of oxygen, corrosion rates of the steel anodes dropped to negligibly low values. With cells operating under the depolarizing action of atmospheric oxygen, the steel anode was found to suffer little or no corrosion by local action. This was indicated by the observation that for periods up to three months the weight losses corresponded, within experimental accuracy limits, to the total amount of current flowing between the platinum and steel elec-

trodes. The corrosion of the anodes was general and no pitting attack was observed. After prolonged periods of corrosion, the anodes had an etched appearance similar to that of steel corroded by strong acid.

In the laboratory experiments illustrated in Figure 2, the corrosion current could be reduced by means of an external resistance and the potentials of the two electrodes measured as a function of the current flowing. Typical polarization curves are shown in Figure 3. It is seen that the anode shows relatively slight polarization, 0.06 volt, with an anode current of 580 microamperes, which corresponds to a corrosion rate of approximately 100 mils/yr. This is therefore a system which satisfies the first requirement for using the potential break criterion of complete protection.

The current vs potential break criterion is shown to be valid for this system in Figure 4 where the anode and cathode potentials are plotted as a function of cathodic protection current. It will be seen that a break occurred in both electrode potential curves when the measured corrosion current between the electrodes fell to zero. The plot of log current vs mean potential is shown in Figure 5. The logarithmic plot shows some curvature near the break but the intersection of the straight line portions of the curve predict the current of complete protection with acceptable accuracy.

A second series of experiments was made using galvanic cells similar to those described above, but with a group of such couples arranged to simulate the corrosion of a long string of casing which would have at least several connected cells. A schematic plan of the apparatus used is shown in Figure 6. Three steel-platinum couples, each operating as a corrosion cell through a milliameter, were connected externally through variable metallic resistances (R_1 and R_2), and cathodic protection currents were applied to the ensemble, the connection being made to the first cell of the group. For this purpose, three additional platinum electrodes were immersed in the drilling mud electrolyte in positions such that the same resistance (R_G) was established between each platinum electrode and its respective corrosion cell. The relative spacing of the electrodes was as shown in the diagram. These platinum electrodes were connected electrically, and protection currents were applied simultaneously from each electrode. The corrosion currents and individual electrode potentials were measured in the same way as that described for the single cell experiments.

In the field, the distribution of the protection current along the casing depends upon the ratio of resistance of the casing to resistance of formation. This is equivalent in the experiments described to the ratio of R_1 and R_2 to R_G.

The experimental procedure adopted was to vary the ratio of R_1/R_G and to study the corrosion currents of the individual anodes and the potentials of selected electrodes as a function of the applied protection current. The data were plotted as the potential of the given electrode vs the logarithm of the applied protection current. It was found that these curves could be divided conveniently into three
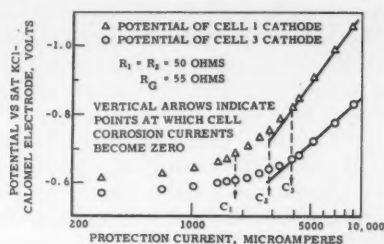
Figure 8—"Average well" model cathodic protection log current-potential curve.
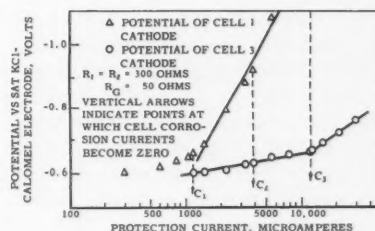
Figure 9—Model for well of extreme depth-cathodic protection log current potential curve.

types: (a) $R_1 = R_2 << R_G$, (b) $R_1 = R_2 = R_G$, and (c) $R_1 = R_2 >> R_G$. These three would correspond in the field to (a) a shallow well, (b) a well of depth found commonly in the Ventura Field, and (c) an extremely deep well. Measurements taken at Ventura confirmed this correspondence. Typical curves for these three ranges are shown in Figures 7, 8, and 9, respectively. In each of these graphs the cathode potential of cell 1 (corresponding to the potential measured at the wellhead) and the potential of the cell 3 cathode (corresponding to a potential near the bottom of the oil string) are plotted against the logarithm of the protection current. Additional data on cell 2 were obtained and were intermediate between those of cells 1 and 3, but are omitted in Figures 7, 8, and 9 for clarity. In most instances, only the cathode potentials were measured since these adequately describe the system.

It is seen from Figure 7 that in the case where $R_1 = R_2 << R_G$, all three corrosion currents became zero over a small range on the curved portion of the cell 1 cathode potential plot. In the experiment reported, the cell currents did not become zero in the order of their numerical arrangement because of differences in the initial corrosion currents and the interaction between the cells as the protection current was applied. Such protection of the cells in an unpredictable order was found only in cases where metallic resistance was low compared to electrolyte resistance, allowing the whole system to be protected over a small range of applied current.

For the case of $R_1 = R_2 = R_G$, illustrated in Figure 8, the cell currents became zero in the expected order. In this case, however, it is clearly demonstrated by the upper (wellhead) curve that the whole system is not completely protected until the final linear part

of the curve is reached. The lower curve (corresponding to the bottom of the casing) in this figure, which is a plot of the cell 3 cathode potential vs log current, shows the same effect. For the conditions illustrated in Figure 9, when $R_1 = R_2 >> R_G$, it can be seen that the cell 1 cathode curve gives very little information concerning the protection of cells 2 and 3. The cell 3 potential curve gives the correct indication of total protection, the final cell current becoming zero at the break point of this curve.

The experiments show that for a single galvanic cell the intersection of the two linear parts of the log current vs potential plot properly indicates the minimum current required for complete protection. However in cases where a group of cells was used the total system was not always protected until the final linear section of the cell 3 log current vs potential plot was reached. The group of cells used corresponds to any corroding structure having separated multiple couples with varying resistances in their respective protection current circuits. It appears therefore that when the potential break criterion is used, instead of taking the intersection of the two straight line portions of the curve as defining the current of complete protection, the point at which the curve becomes linear is the proper choice.

Discussion

A graphic explanation of the modification suggested for the potential break criterion can be illustrated by the model shown in Figure 10 (a). The diagram represents a corroding structure with anodic and cathodic areas distributed along it. For the purpose of demonstration these areas will be designated as cell 1, cell 2, . . . cell n, separated by metallic resistances R_1, R_2 . . . R_n. Current is drained through a connection to cell 1 from an external source (A). The total current (C) is collected from each cell as C_1, C_2, . . . C_n, these currents being progressively smaller fractions of the total current (C).

Assume that the potential (P) of the structure surface at each cell location is a logarithmic function of the current density in the surface; for example, considering unit areas of each cell, $P_x = P_o + k_1 \log C_x$. Assume further that at the current of complete protection k_1 changes abruptly to another value, k_2. These assumptions are reasonable in view of the findings for a single galvanic cell.

Then if P_1, P_2 . . . P_n are plotted against the logarithm of total current (C), a group of curves as shown in Figure 10 (b) would be obtained. If the potential of this structure is measured with reference to an external electrode, an average of P_1, P_2 . . . P_n is obtained, the contribution of each potential element depending upon the geometry involved in the location of the reference electrode. An average potential curve is shown as the broken line in Figure 10 (b). It is clear that curvature continues and the total system is not protected until the average potential curve finally becomes a straight line. A similar result is obtained if one considers a model of a corroding system with multiple couples having anode and cathode films of various resistances.

Comparison of Laboratory Results with Field Data

Owing to differences in the systems studied, the actual values of potentials measured in the laboratory experiments were not significant for comparison with field data. Protection was achieved in the laboratory experiments when the galvanic couples reached a potential of approximately — 0.68 volt with respect to a saturated KCl — calomel electrode (i.e., — 0.7; for the Cu—CuSO$_4$ electrode.) This is significantly below the value of — 0.85 volt (Cu—CuSO$_4$) used in protection criterion (1) discussed previously. Since, as has been stated earlier, the open circuit potential of a steel anode will depend on its environment, it is to be expected that the value of the protection potential measured in the laboratory environment would be different from that experienced in underground formations.

The laboratory curves could be compared with field curves with respect to their shapes and to the relative displacement between the wellhead and bottom of casing potential curves along the protection current axis. The log current vs potential curves obtained on a typical Ventura Field well are shown in Figure 11. From the 8000 feet curve shown in this figure, it is estimated that the casing at this depth is protected by a current of approximately 27 amperes. The same criterion applied to the wellhead curve indicates a required current of 19 amperes. From comparisons with a large number of field curves, it was concluded that the resistance ratios controlling current distribution at Ventura are similar to those which give rise to curves of the type shown in Figure 8, tending slightly to that shown in Figure 9. It is clear that "bottom hole" potential curves must be used to indicate protection to the bottom of the well. This point is particularly emphasized by the laboratory experiments illustrated in Figure 9. In practice, owing to the cost of obtaining "bottom hole" curves, it is desirable to use wellhead curves wherever possible. This can be done after sufficient "bottom hole" data have been obtained to establish the pattern of current distribution existing in any particular field. In the case of shallow wells, the experimental data indicate that wellhead curves can be used satisfactorily.

Using the modified potential break criterion, comparisons for approximately 60 wells in the Ventura Field have indicated required protection currents ranging from 21 to 37 amperes. It is interesting to note that, if the modified criterion is applied to the curves presented by Ballou and Schremp[8] for wells at Kettleman Hills, California, protection currents are indicated closely corresponding to the 1.5 ma/sq ft criterion used by these authors.

Conclusions

In conclusion, there are two features which add to the attractiveness of cathodic protection as a means of combating casing corrosion. The first of these is the more permanent polarization effects accompanying prolonged protection treatments. Such effects have been shown by the experiments of Barrett and Gould[4] and Ballou and Schremp.[8] The second effect is the non-proportionality of the amount of corrosion
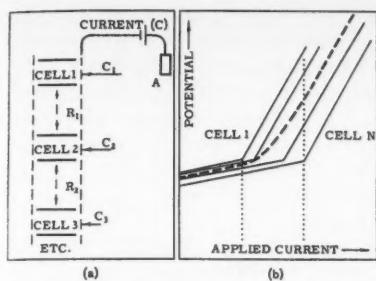
Figure 10—Model to illustrate modification of potential break criterion in multiple cell application.
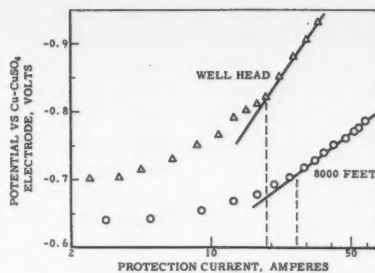
Figure 11—Log current-potential curves for typical Ventura well.
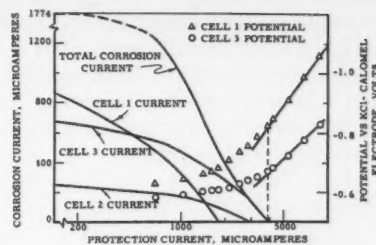
Figure 12—"Average well" model corrosion current as a function of the protection current.

supressed to the protection current applied. The corrosion suppressed as a function of applied protection current can be estimated from the laboratory data. Figure 12 shows the cell 1 and cell 3 cathode potential curves as given in Figure 8 for the "average well" model. In addition, the corrosion currents of the individual cells and the sum of these three currents are shown as a function of the applied protection current. It will be seen that 75 percent of the current required to give complete protection will suppress 90 percent of the total corrosion. In Figure 12, a protection current of 3000 microamperes completely protects cells 1 and 2 and suppresses more than 75 percent of the cell 3 corrosion current.

The long term polarization effects and the disproportionality of corrosion suppressed to current applied ensure that slight underestimation of the current required for complete protection will not affect seriously the over-all economics of an installation.

Acknowledgment

The author wishes to express his appreciation to A. Wachter, G. G. Eldredge, and R. S. Treseder for helpful suggestions and discussions during the course of the work reported and in the preparation of this paper. He also takes pleasure in acknowledging the cooperation of Shell Oil, Ventura personnel who obtained the field data referred to in the text.

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DISCUSSION

Questions by James E. Landers, Continental Oil Company, Ponca City, Oklahoma:

Was any special procedure followed in positioning the reference electrode during field measurements? Was the conventional "interrupter" method used in obtaining the log current-potential curves?

Replies by E. W. Haycock:

The reference electrode was positioned opposite the anode beds 200-260 feet from the well. The conventional "interrupter" method was used.

Question by Roland E. Bussell, Freeport, Texas:

Was there evidence of severe corrosion at those greater depths to warrant additional cost of current drainage from 3 amperes to 30 amperes?

Reply by E. W. Haycock:

A statistical analysis of the occurrence of casing leaks with depth in the Ventura Field has shown no preferred location of corrosion. Although current drainage in excess of 30 amperes is indicated to achieve complete protection for some wells at Ventura, an over-all economic evaluation has led to the decision to apply 27 amperes to all wells.

Questions by A. H. Roebuck, Continental Oil Company, Ponca City, Oklahoma:

Can we assume that the anodic reactions change from one of oxidation to one of reduction as cathodic protection is achieved? In your studies did you use any special technique to study the electrode re-

actions, and changes incurred by cathodic protection current? Some studies have shown that local corrosion currents remain even after high cathodic protection currents have been applied. For this reason, any elucidation of the changes in anodic and cathodic currents and anodic and cathodic areas would be of great potential interest.

Replies by E. W. Haycock:

In the iron-platinum system studied, the reversal of current flow to the iron anode was interpreted as indicating the achievement of cathodic protection. The reversal of current requires a change of electrode reaction from one of oxidation to one of reduction. Local corrosion currents at the iron anode were not studied under conditions when the total current to the anode was zero. When the iron-platinum couples were allowed to corrode freely, the anode lost iron uniformly and hence local currents under these conditions were insignificant.

No attempt was made to study the electrode processes in detail.

Questions by Gordon L. Doremus, Cathodic Protection Service, Houston, Texas:

In Figure 11, where field tests on a given well gave a current-potential break at approximately 18 amperes for a contact at the well head and 27 amperes for bottom hole contact, was the reference electrode at the same point in each case? Under such circumstances, would not a portion of the indicated spread between test results be attributed to the fixed, relatively close reference electrode spacing from the well head (i.e., would not a more remote electrode (5000′ ±) reduce the indicated spread between current drains at top and bottom of the well?)

Reply by E. W. Haycock:

The reference electrode was at the same location for both the wellhead and bottom hole measurements. The detailed techniques used in the field measurements have been reported recently.[1]

Since measurements were taken with the protection current interrupted, differences in IR terms included in the readings obtained for a wellhead and bottom hole contact would depend upon the pattern of corrosion currents existing in any particular case. These corrosion currents could lead to discrepancies in either direction in the potentials measured but would have a much reduced effect on the shape of the current potential curves. The differences measured in the two positions can be accounted for more realistically on the basis of the casing resistance rather than on the basis of the anomalies produced by inclusion of IR terms in the measured potentials.

[1] Alex Kerr. Cathodic Protection of Casing—Ventura Field. API Paper No. 801-33-G, presented at Spring meeting of API Pacific Coast District, Division of Production, Los Angeles, May 16-17, 1957.

Fundamentals of Electrode Processes in Corrosion*

By MILTON STERN

Introduction

THE MAJORITY of corrosion reactions in aqueous environments occur by an electrochemical mechanism. So many factors affect the distribution, rate, and mode of corrosion that selection of an appropriate material for a particular application requires a sound understanding of the fundamental processes which occur during chemical attack.

Recent advances in the theory of electrode kinetics provide a simple means for explaining many of the experimental observations made in the corrosion field. This discussion is an effort to bridge the gap between the thinking of the electrode kineticist and the practicing corrosion engineer.

Fundamentals of the Corrosion Process

In the corrosion process, metal atoms in a crystalline lattice are transformed to metal ions in the corrosion environment in accordance with the reaction $M \rightarrow M^+ +$ electron. This is a chemical oxidation. By definition, this process occurs on an area of the metal surface called an anode. An oxidation of the type written above cannot occur without a corresponding reduction reaction somewhere in the system. The reduction reaction consumes electrons and by definition occurs at cathode areas.[1] Both the oxidation reaction and the reduction reaction proceed at the same rate during electrochemical corrosion. Any change in the system which affects the rate of one must of necessity affect the other. Thus, attempts at reducing corrosion rates may be directed toward changing either local oxidation or local reduction rates.

The Anodic Process

The most apparent first approach to reduction of corrosion is to attempt to reduce the net rate of oxidation since this is synonymous with the actual metal dissolution reaction. If one considers a metal with some given inherent tendency to go into solution, the most obvious method for changing this tendency is to introduce alloying elements into the metallic structure. This approach has lead to the development of many special alloys which exhibit remarkable corrosion resistance in very aggressive environments. The design of such alloys generally does not fall within the realm of the practicing corrosion engineer, and thus this aspect of corrosion prevention shall not be considered further.

MILTON STERN is a Research Metallurgist at the Metals Research Laboratories, Electro Metallurgical Company, Union Carbide Corporation, Niagara Falls, New York. He received a BS in chemical engineering at Northeastern University and an SM and ScD from Massachusetts Institute of Technology in physical metallurgy. He was Weirton Post-doctoral Fellow at the corrosion laboratory of MIT for two years prior to joining the Metals Research Laboratories. Dr. Stern was presented the Young Authors Award of the Electrochemical Society in 1955. He is a member of ACS, AIME, ASM, The Electrochemical Society, and NACE.

Abstract

Recent advances in the theory of electrode kinetics provide a simple means for explaining many of the experimental observations made in the corrosion field. The concepts of exchange current, activation polarization, and concentration polarization are introduced in an effort to bridge the gap between the work of the electrode kineticist and the practicing corrosion engineer. Many of the early classic experiments in the field of corrosion are discussed along with modern observations of the effects on corrosion rate of solution velocity, galvanic coupling, and metal and environment composition. **3.8.2**

The Cathodic Process

The cathodic process is most important to the man in the field because physical and chemical factors in the environment markedly affect the rate of electrochemical reduction. A thorough knowledge of the manner in which the corrosion rate is affected by the cathodic process is most important to successful design and material selection. To illustrate this, it is convenient to resort to a modification of the classical polarization diagram for a corroding metal, presented in Figure 1. The open-circuit potentials[2] of the anodic and cathodic processes are labeled E_A and E_C, respectively. Since neither the cathodic nor the anodic processes are at equilibrium, the potentials of the local elements of the corrosion cell are polarized. Polarization may be defined as the change in potential of an electrode which results from current flow to or from the surface. It is important to realize that current flow is synonymous with oxidation or reduction rate in electrochemical corrosion. Thus, when

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[1] Electrochemical theory considers that anodes and cathodes exist as discrete areas on a metal surface. These areas are large compared with atomic dimensions. The distribution of anode and cathode areas often fluctuate with time, producing uniform attack in spite of the fact that metal solution occurs only at the anodes.

[2] The open-circuit potential of the anodic process is the equilibrium potential of the metal system calculated from thermodynamic considerations. For corroding iron, for example, the process would be iron atoms in equilibrium with ferrous ions, $Fe \rightleftarrows Fe^{++}$. The cathodic process is dependent upon the corroding environment. In a reducing acid, the reaction will be the reduction of hydrogen ions and the reversible potential will be that of a hydrogen electrode in the same solution.
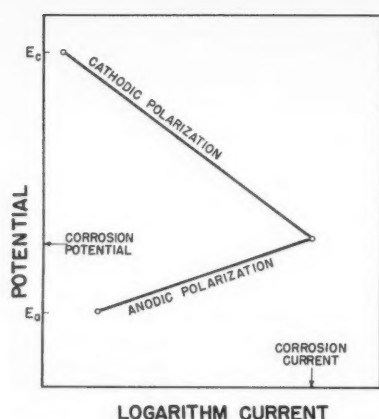
Figure 1—Polarization diagram for a corroding metal.
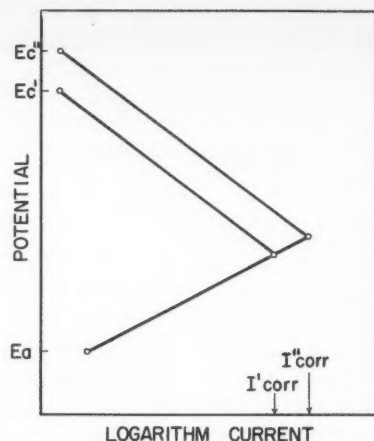
Figure 2—Effect of concentration changes on cathodic activation polarization and corrosion rate.
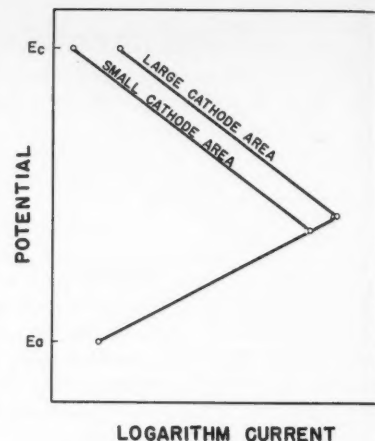
Figure 3—Effect of cathode area on the position of the cathodic activation polarization curve and the corrosion rate.

one refers to a given current flow, the actual process at the electrode surface consists of an equivalent rate of oxidation or reduction.

Measurement of the potential of a corroding metal yields a value which lies somewhere between the equilibrium (calculated) values of the reversible potential of the oxidation-reduction systems which are operative. This corrosion potential, indicated in Figure 1, is dependent upon the shape of the local anodic and cathodic polarization curves and is determined by the intersection of these curves. The local anodic current at this potential is equivalent to the corrosion rate.

Activation and Concentration Polarization

Since the shape of the anodic polarization curve may be considered characteristic of a particular metal system, it is advantageous to consider those environmental factors which influence the shape of the local cathodic polarization curve. The rate of electrochemical reduction at a cathode surface is basically controlled by two factors.[3] The first is the activation energy required to change the species being reduced at the cathode from its oxidized to its reduced state. The second factor which is often important is the rate of diffusion toward the cathode surfaces of the ions being reduced. Experiment shows that activation control results in a polarization curve which is a logarithmic function of current. That is, a straight line results when cathode potential is plotted as a function of current.

Factors Affecting Activation Polarization

Activation polarization is a function of the nature and concentration of the species being reduced, surface roughness and composition, and temperature. In addition it is sensitive to traces of reducible impurities in the system.

Figure 2 illustrates how a change in concentration of the species being reduced may affect the corrosion

rates by changing activation polarization characteristics. An example of this is an increase in acid concentration during the corrosion of metals such as iron, zinc, and nickel. An increase in hydrogen ion concentration, or a reduction in pH, will move the open-circuit, cathode potential in a cathodic direction. Assuming the shape of the polarization curve remains constant, the corrosion potential will become more cathodic and the corrosion rate will increase from i'_{corr} to i''_{corr}.

If the cathode area is made rough, so that the effective area for reduction is increased, the corrosion rate is affected in the manner illustrated in Figure 3.[4] The open-circuit cathode potential is not affected. The cathodic polarization curve is shifted to the right intersecting the local anodic polarization curves at a higher current. This phenomenon exists because polarization is actually a function of current density. Thus, at the equilibrium potential, E_c, more total current flows. The current or reaction rate at the equilibrium potential is often called the exchange current for the following reason: At an electrode at equilibrium, the reacting species is being oxidized and reduced at the surface at equivalent rates. There is a continuous exchange in oxidation-reduction state among the reacting ions. This current exists regardless of whether corrosion occurs. The system at equilibrium may be designated by the reaction
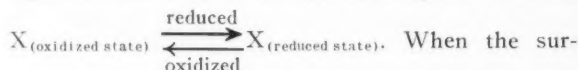
$$X_{(oxidized\ state)} \underset{oxidized}{\overset{reduced}{\rightleftharpoons}} X_{(reduced\ state)}.$$ When the surface functions as a cathode in a local corrosion cell, the rate of reduction far exceeds the rate of oxidation and usually one need consider only the reduction reaction.[5]

Impurities present in a corroding environment are often plated out onto cathode areas of a corroding

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[3] It is important to realize that rate of reduction and cathodic current flow as illustrated in Figure 1 are synonymous.

[4] Actually, roughening the cathode surface may result in other changes. However, these are not discussed for the sake of simplicity.

[5] In all this discussion, the local polarization diagrams illustrated include only the reduction reaction at the cathode and the oxidation reaction at the anode.
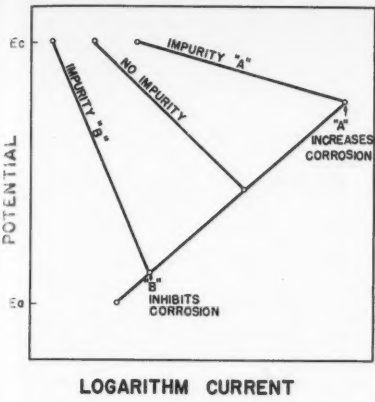
Figure 4—Effect of impurities on cathodic activation polarization and corrosion rate.
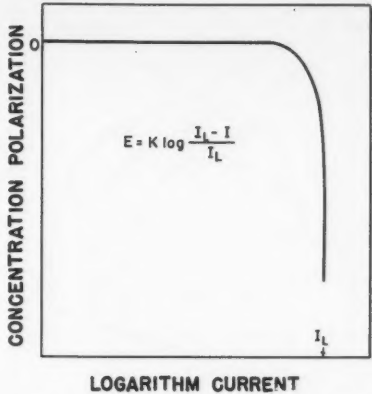
Figure 5—The shape of a concentration polarization curve.
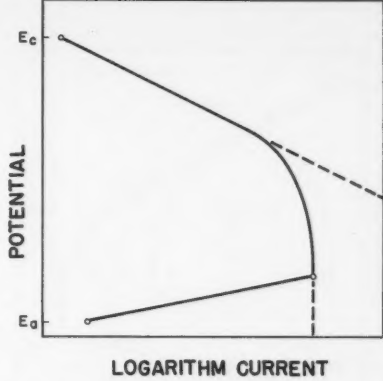
Figure 6—Cathodic polarization curve where both activation and concentration polarization are significant.

metal as a result of the local action current which flows between anodes and cathodes. This may have a marked influence on the position of an activation overvoltage curve. Both the exchange current (the current at which the polarization curves start) and the slope of the polarization curve will be changed.[6] The combination of these two changes may result in either an increase or decrease in corrosion rate. Figure 4 illustrates this. Impurity A is assumed to increase the exchange current and decrease the slope of the cathodic polarization curve. This results in an increase in corrosion rate. Impurity B is assumed to decrease the exchange current and increase the slope, causing a decrease in corrosion rate. Impurity B thus functions as a corrosion inhibitor.

Factors Affecting Concentration Polarization

As mentioned previously, the rate of reduction of a substance at a cathode may be limited by the rate of diffusion of the reaction species to the surface. The change in potential under these conditions is called concentration polarization. The shape of the polarization curve is not that illustrated for activation polarization. The curve is defined by an expression of the type $E = K \log \frac{I_L - I}{I_L}$ where K is a constant. The limiting diffusion current, I_L, is equivalent to the maximum rate of diffusion of the reacting species to the surface, and I is the cathodic current. The shape of such a curve is shown in Figure 5. When I is very small in comparison to I_L, concentration polarization is negligible. When I approaches I_L in magnitude, concentration polarization approaches infinity.[7] In nature, it is doubtful that concentration polarization occurs without some activation polarization so that the actual local cathodic polarization curve of such a system would consist of the summation of the two curves. This is illustrated in Figure 6.

Concentration polarization is affected by those environmental influences which change the rate at which a species being reduced can reach the cathode surface. The two most important factors in this connection are the environment velocity adjacent to the cathode surface and the concentration of the diffusing species in the environment. An increase in velocity increases the maximum diffusion rate in much the same manner that an increase in velocity increases the rate of heat transfer through a metal interface. The two systems may be considered analogous. Thus, an increase in solution velocity increases the limiting diffusion current, I_L, and shifts the steep portion of the concentration polarization curve to higher currents. The effect of an increase in velocity on corrosion rate is illustrated in Figure 7.

An increase in the concentration of the species being reduced increases the maximum rate at which it can diffuse to the cathode surface because this increases the concentration gradient. Thus I_L is increased. As already mentioned, the open-circuit cathode potential also is changed by a concentration change. Figure 8 shows the effect of such concentration changes on corrosion rate.

Simultaneous Cathodic Processes

Very often in practice more than one species in solution is reduced at the cathode of a corrosion cell. An example of this would include a metal corroding in an acid containing oxygen, ferric ions, or some other easily reducible component. In a system of this type, both hydrogen ions and the oxidizing agent are reduced at cathode surfaces. The rates of each reduction may be considerably different. In addition, each reduction reaction will exhibit its own individual polarization characteristics, the resulting local cathodic polarization curve for the system being the sum of the two individual reactions.

Figure 9 illustrates an example of this where species Y is representative of the behavior of a reducible constituent such as oxygen. Both activation

[6] Adsorbed or electrodeposited impurities will produce this effect because they either change the activation energy required to reduce the reacting ion or they produce a new surface with entirely different electrochemical properties.

[7] The potential never becomes infinite, of course, since a potential region is reached where a different reaction will become predominant.

Figure 7—The effect of velocity on the limiting diffusion current and the corrosion rate.
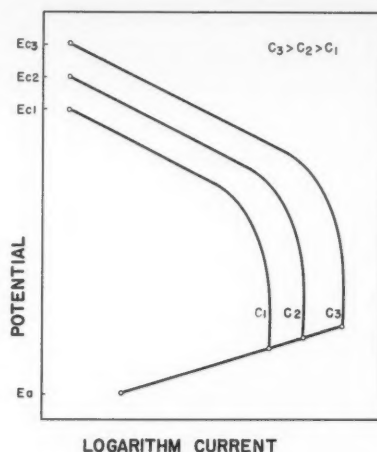
Figure 8—The effect of concentration on the limiting diffusion current and the corrosion rate.
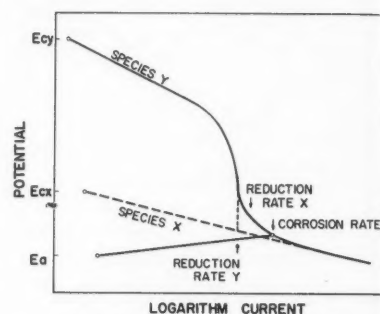
Figure 9—Polarization diagram where two simultaneous reduction reactions occur.

and concentration polarization are included in the polarization curve. Species X is representative of the reduction of hydrogen ions to form hydrogen gas. Only activation polarization is considered here.[8] It is important to note the different exchange currents for the various electrode processes indicated in Figure 9. The local anodic polarization curve intersects the sum of the two cathodic curves at the corrosion current labeled on the curve. For the system illustrated, the rate of reduction of X is greater than the rate of reduction of Y. This is also shown on the figure by indicating the currents which are equivalent to the reduction rates of X and Y. Note that the rate of reduction of Y is equivalent to the limiting diffusion current. The corrosion current equals the sum of reduction current of X and Y.

Figure 10 shows a system with the same cathode polarization behavior as Figure 9 but with a different anodic polarization curve. In this case, the reduction rate of Y is considerably greater than the reduction rate of X and the corrosion rate is practically equivalent to the limiting diffusion current of Y.

The system described in Figure 9 is representative of iron corroding in aerated acid solutions where hydrogen evolution occurs. Figure 10 is equivalent to the corrosion of iron in nearly neutral aerated solutions where the reduction of oxygen is the predominant cathodic reaction.

Application of Fundamentals to Experimental Observations

To illustrate more clearly how these principles apply to practice, it is convenient to discuss some of the classic, early experiments conducted in the corrosion field, and illustrate how these are explained in terms of the fundamental principles which have been presented. For the sake of simplicity, the discussion shall be limited to corrosion of iron and steel.

Effect of pH on Corrosion Rate

Whitman and Russel[1] determined the effect of pH on the corrosion rate of mild steel in Cambridge, Massachusetts, tap water. The corrosion rate was determined by measuring the consumption of oxygen due to the corrosion reaction.[9] They reported that the corrosion rate was constant between about pH 9 and pH 4. As the water was made even more acid, the corrosion rate rose sharply between pH 4 and pH 2.

This system may be considered one where the corrosion rate is determined by the maximum rate at which oxygen can diffuse to the surface; that is, by the limiting diffusion current for oxygen. In the pH range 9 through 4, the iron surface is covered by insoluble corrosion products. Increasing the hydrogen ion content does not affect the limiting oxygen diffusion rate. As the solution is made more acid (pH decreased from 4 to 2), the corrosion product film dissolves removing one of the barriers to oxygen diffusion. Thus, the oxygen limiting diffusion current increases giving rise to a rapid increase in the corrosion rate. The local polarization diagram is basically that presented in Figure 7. Between pH values of 9 and 4, the position and shape of the local cathodic polarization curve are not affected. Between pH values of 4 and 2, the steep portion of the polarization curve is shifted progressively to higher current values.

Effect of Oxygen Concentration on Corrosion Rate

Many investigators have determined the effect or dissolved oxygen in various environments on the corrosion rate of different metals and alloys. Excluding systems which exhibit passivity phenomena, the experimental results show a linear dependence of corrosion rate on oxygen content. It is well known that neutral water containing no oxygen corrodes iron at an insignificant rate at room temperature. Cox and

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[8] Concentration polarization can also occur for this process. It is eliminated to simplify the presentation.

[9] The investigators found a negligible amount of hydrogen evolution in the pH region investigated.
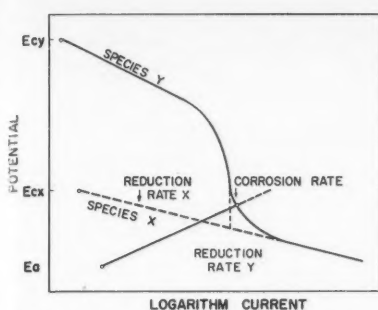
Figure 10—Effect of anodic polarization on the relative rates of reduction of two simultaneous cathodic reactions.
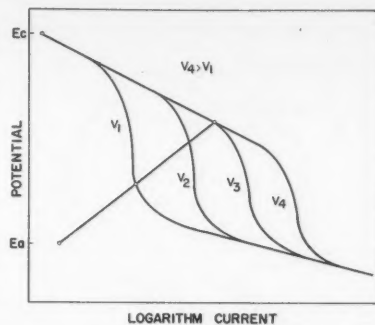
Figure 11—Effect of the position of the local anodic polarization curve on the influence of velocity on corrosion rate.
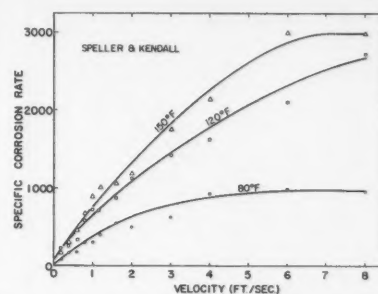
Figure 12—Effect of water velocity on the corrosion rate of one-half inch iron pipe (Speller and Kendall[8]).

Roetheli[2] show the linear increase in corrosion rate of steel as the oxygen content of water is raised. For a diffusion-controlled process, an increase in concentration of the diffusing species in the bulk of the environment increases the concentration gradient at the metal interface. The concentration gradient provides the driving force for the diffusion process. Thus, the maximum rate at which oxygen can diffuse to the surface (the limiting diffusion current) would be essentially directly proportional to the concentration in solution. Figure 8 is an example of the type of cathodic polarization diagram which is operative for this system.

It is interesting to note that one aspect of boiler maintenance requires that the oxygen content of the feed water be kept at a minimum.

Effect of Environment Velocity on Corrosion Rate[10]

Velocity primarily affects corrosion rate through its influence on diffusion phenomena. It has little effect on activation controlled processes. The manner in which velocity affects the limiting diffusion current is a marked function of the physical geometry of the system. In addition, the diffusion process is affected differently by velocity when flow conditions are laminar as compared to a situation where turbulence exists.[4] All the possible geometric situations which the corrosion engineer finds have not been worked out. For flow past a flat plate set into a laminar flow of liquid the limiting diffusion current is proportional to the square root of velocity. It is inversely proportional to the square root of the distance from the leading edge of the plate.[5] For turbulent flow under these conditions the limiting diffusion current is proportional to the velocity raised to the 0.9 power.[6]

For a disk revolving about an axis passing through its center, Levich[6] found the limiting diffusion current was proportional to the square root of the angular velocity of the electrode.

For most conditions, the limiting diffusion current can be expressed by the equation:

$$I_r = KV^n$$

where K is a constant, V is the velocity of environ-

ment relative to the surface and n is a constant for a particular system. Values of n vary from 0.2 to 1.0.[7]

The corrosion rate would be directly proportional to the limiting diffusion current until the intersection of anodic and cathodic polarization curves occurs at a current less than the limiting diffusion current. At higher velocities, the corrosion rate would be relatively independent of velocity until cavitation or erosion changes the physical conditions of the system. This is illustrated in Figure 11. For velocities up to V_3, the corrosion rate and limiting diffusion current are proportional to the velocity in the manner described above. At velocities higher than V_3 the corrosion rate is independent of velocity until mechanical disturbances completely change the shape and position of the local polarization curves. Figure 12 is a plot of data obtained by Speller and Kendall[8] who measured the effect of velocity of aerated water on the corrosion of ½-inch iron pipe. Qualitatively, the shape of the curves is similar to the effects found by several other investigators.[2,9] The corrosion rate increases in a somewhat linear manner as the velocity increases until higher velocities are reached. In this region, the effect of velocity is not so pronounced. If the corrosion rate is determined by the limiting diffusion current for oxygen, then the rate should be proportional to V^n. This can be tested by plotting the logarithm of the corrosion rate as a function of the logarithm of velocity. The data of Speller and Kendall illustrated in Figure 12 are plotted in this manner in Figure 13. The constant, n, in this case turns out to be 0.79. Note at the highest velocities that the rate no longer increases as $V^{0.79}$. Under these conditions, the situation is probably best described by Figure 11 which, as discussed earlier, illustrates why further increases in velocity have no significant effect.

Effect of Iron Composition and Heat-Treatment on Corrosion Rate

As mentioned earlier, cathodic processes are activation- and/or diffusion-controlled. If the reaction is controlled primarily by the rate of diffusion of a reacting species from the environment to the surface, it becomes obvious that the chemical and physical nature of the surface are not significant factors in

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(10) This discussion does not include systems where erosion, cavitation or passivity is predominant factor. An excellent review of the effects of velocity on corrosion by water is presented by Copson.[9]
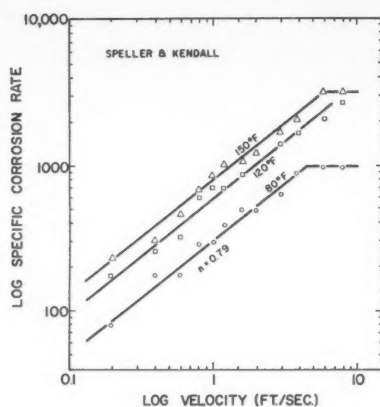
Figure 13—Logarithm of corrosion rate as a function of the logarithm of water velocity for one-half inch iron pipe (Speller and Kendall[5]).
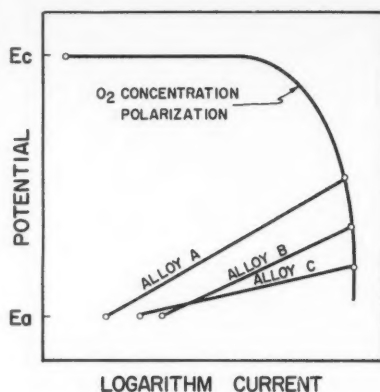
Figure 14—Effect of small differences in metal composition and heat-treatment on corrosion rate where cathode concentration polarization predominates.
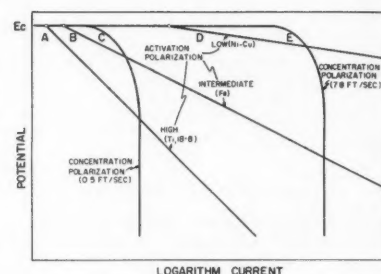
Figure 15—Local cathodic activation and concentration polarization curves for the metals listed in Table 1.

the process. LaQue[10] has shown that in sea water there is no significant difference in corrosion rate between wrought iron, plain carbon steel, copper steel, and a 2 percent nickel steel. Uhlig[11] illustrates a similar situation for distilled water and 3 percent sodium chloride. Thus, while the local anodic process may be considerably different for the different steels, the corrosion rate is the same. This situation, in terms of local polarization diagrams, is illustrated in Figure 14. The cathodic polarization curve is illustrated as oxygen concentration polarization with a negligible contribution from activation polarization. It is evident that the corrosion rate is the same for the different materials because of the steep nature of the local cathodic polarization curve at the limiting diffusion current. Actually, Wormwell[7] reports that hydrogen evolution accounts for about 5 percent of the total cathodic process when steel is corroded in moving sea water. In hard water or in 0.5N NaCl, the proportion of hydrogen evolution is smaller. This points out, however, the necessity for considering all the possible reduction reactions which may occur. Figure 10 is an illustration of Wormwell's system where the majority of the reduction reaction is oxygen consumption indicated as species Y and a small fraction of the total cathodic current consists of hydrogen evolution, indicated as species X.

The rate of hydrogen evolution would be a function of the composition of the steel because the position and shape of the hydrogen activation polarization curve are dependent upon such factors. In the experiments described by LaQue,[10] this factor is masked by the more significant rate of oxygen reduction. Evans[12] points out the importance of metal purity in acid solutions by showing that the corrosion rate of gray pig iron is one hundred times as large as the rate of electrolytic iron in one normal hydrochloric acid. In general, composition, heat-treatment, and structure will play an important role in corrosion when activation overvoltage predominates over diffusion control.

Table 1—Effect of Velocity on Galvanic Corrosion of Steel in Sea Water[2]

COUPLE	Velocity 0.5 Ft/Sec		Velocity 7.8 Ft/Sec	
	Corrosion Rate, mdd	Galvanic Effect, mdd	Corrosion Rate, mdd	Galvanic Effect, mdd
Steel	60	..	170	..
Steel to 18-8	141	81	195	25
Steel to titanium	139	79	224	54
Steel to copper	119	59	525	355
Steel to nickel	117	57	607	437

Note: (Temperature 50 F; Time 16 to 19 days; Areas 0.2 sq dm.)

Galvanic Couples

It is well known that contact between dissimilar metals in a corrosive environment often leads to accelerated attack of the more active material. The fundamental behavior of galvanic couples has been thoroughly discussed by Wesley and Brown[13] and the details need not be repeated here. However, such systems permit more extensive discussions of the role of cathodic processes in determining corrosion reactions and only this aspect will be mentioned.

Copson[3] shows some interesting data obtained by LaQue on the effect of sea water velocity on galvanic corrosion of steel coupled to stainless steel, titanium, copper, and nickel. The results are reproduced in Table 1.

In such a system, both oxygen concentration polarization and activation polarization play an important role. The materials coupled to steel would all yield similar results if oxygen diffusion alone controlled the galvanic current. Actually, this appears to be the case for the results at 0.5 ft/sec. The galvanic effect, which is the increase in corrosion rate of iron which results from being coupled to another metal of equal area, is essentially constant and is approximately equal to the corrosion rate of uncoupled steel. The cathodic reaction rate is thus practically the same on all surfaces which indicates that the reduction rate of oxygen is proceeding at the maximum rate determined by diffusion. The various surfaces differ, however, in respect to activation polarization of oxygen. This causes the marked dif-
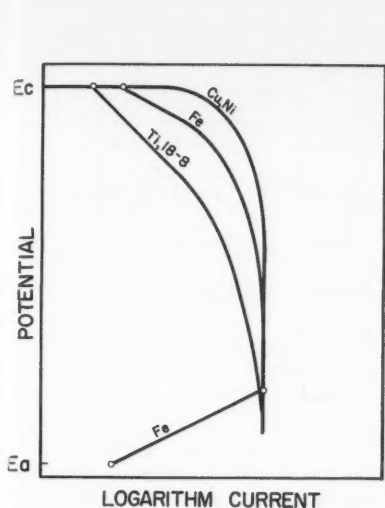
Figure 16—Local cathodic polarization curves at 0.5 ft/sec for the metals listed in Table 1.
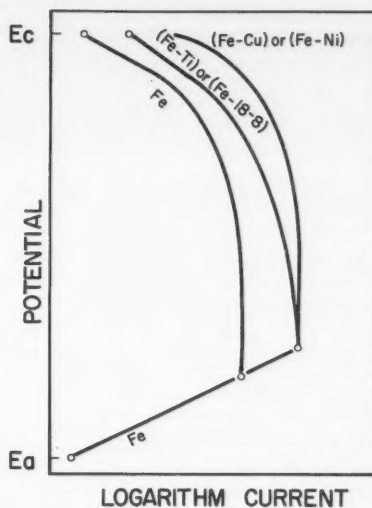
Figure 17—Local cathodic polarization curves at 0.5 ft/sec for the galvanic couples listed in Table 1.
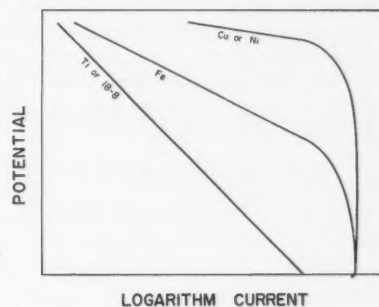
Figure 18—Local cathodic polarization curves at 7.8 ft/sec for the metals listed in Table 1.

ference at 7.8 ft/sec between titanium and 18-8 stainless steel as compared to copper and nickel.

An explanation of the data in Table 1 in terms of polarization diagrams must conform with the following experimental observations:

1. At the low velocity, the galvanic effect is essentially constant for all the couples and is approximately equal to the corrosion rate of steel.

2. At the high velocity, the corrosion rate of steel increases; the galvanic effects of 18-8 stainless and titanium are less than obtained at lower velocities; the galvanic effects of copper and nickel are very much greater than that observed at lower velocities; and finally the galvanic effect of copper and nickel are significantly greater than the corrosion rate of uncoupled steel under the same conditions.

There are several different local cathodic polarization curves which are important in this system. Two of these, oxygen concentration polarization at 0.5 and 7.8 ft/sec, are the same for all the metals. The remaining local polarization curves deal with activation polarization which is different for the different metals.

It is convenient for the sake of simplicity to combine the oxygen activation overvoltage behavior of the metals into three categories—those with high (polarize markedly), intermediate, and low polarization tendencies. Titanium and 18-8 stainless steel are characteristic of materials with high-oxygen overvoltage behavior, steel behaves as an intermediate material, while copper and nickel appear to polarize only slightly.[11]

The five important local polarization curves which are pertinent to the data of Table 1 are presented in Figure 15 and are labeled A through E for conven-

ience of discussion. At a velocity of 0.5 ft/sec, Curve C for oxygen concentration polarization must be added to the activation polarization data to produce the local cathodic polarization curve for the various metal systems. These are plotted on Figure 16. On this plot, the local anodic polarization curve for iron is included. The intersection of this curve and the local cathodic polarization curve for iron occurs at a current equivalent to the corrosion rate of steel in the system.

It is now necessary to consider what happens when steel corroding under these conditions is coupled to another metal. In any system corroding electrochemically, the sum of all the rates of oxidation must equal the sum of all the rates of reduction.[12] That is, the sum of all the cathodic currents must equal the sum of all the anodic currents. In the system under discussion, regardless of whether the steel is galvanically coupled, the total anodic current is equivalent to the corrosion rate. Thus, the effect on corrosion rate of galvanically coupling steel to another metal may be evaluated by summing the rates of reduction of oxygen on both steel and the other metal. This yields the local cathodic polarization curve of the galvanic couple.

Figure 17 shows a plot of such curves for steel coupled to the various materials in Table 1 along with the polarization curve for steel alone. The potential of the couple becomes somewhat more noble than the potential of steel alone and the corrosion rate of iron doubles.[13] The conditions which exist here are exactly those which applied in the classic experiment of Whitman and Russell[14] who exposed steel plates partly coated with copper, to corrosion by water. Those authors found that, regardless of the area of iron coated, the total weight loss of iron

[11] The difference in exchange current for these materials is as significant as the differences in the actual slope of their polarization curves.

[12] This might well be called the "First Law of Corrosion".

[13] It is important to note that the current scale is logarithmic so that it is not readily apparent from the graph that the anodic current has doubled.

was the same as that of bare steel. The corrosion rate is determined by the limiting diffusion current of oxygen to the couple surface.

At a velocity of 7.8 ft/sec, Curve E on Figure 15 for oxygen concentration polarization must be added to the activation polarization data to produce the local cathodic polarization curves for the different metal systems. This is presented in Figure 18. For the galvanic couples listed in Table 1, the local cathodic polarization curve is obtained by suming the reaction rates at any potential. This is shown in Figure 19 along with the local anodic and cathodic polarization curves of iron alone. Point E is indicated at the corrosion current of uncoupled iron. Point F shows the corrosion current of iron coupled to titanium or stainless steel while Point G designates the corrosion current of iron coupled to nickel or copper. Note the relatively small galvanic effect produced by titanium and stainless steel as compared to that which exists when copper and nickel are connected to iron.

Figures 16 through 19 qualitatively explain all the effects reported in Table 1. This sort of analysis is extremely useful in gaining an understanding of the various processes which occur in a corroding system. It also allows one to make predictions of the effects other variables will have on the behavior of a system.

Discussion

The principles discussed here cover only a small fraction of the many phenomena which occur in all corrosion processes. High-temperature oxidation, mechanical factors, localized attack, passivity, protective coatings, and cathodic protection either have been neglected or mentioned only briefly. An extensive analysis of these factors is beyond the scope of this discussion. Many excellent references describing these phenomena are available. An extensive amount of good practical information is available in the literature. Accurate use of this information, however, demands a sound, thorough knowledge of basic principles.

A list of corrosion rates of metals and alloys in a given environment has little value and indeed can be very dangerous unless the user is aware of the many environmental and metallurgical factors which
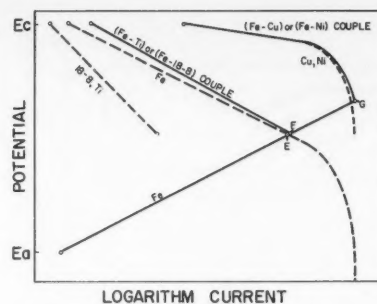
Figure 19—Local cathodic polarization curves at 7.8 ft/sec for the galvanic couples listed in Table 1.

affect the corrosion rates reported. This discussion will have fulfilled its purpose if it has stimulated to some degree the application of basic principles to the solution of practical industrial corrosion problems. Such an approach is guaranteed to pay dividends.

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Canadian, New York Committees Join T-7 Group

Twelve Underground Corrosion Control Units Affiliated

The Southern Ontario Committee on Electrolysis has affiliated with NACE Technical Group Committee T-7 Corrosion Coordinating Committee under Unit Committee T-7F, Canadian Region Corrosion Coordinating Committee.

Officers of the Southern Ontario Committee on Electrolysis are: R. E. Kuster, Union Gas Company of Canada, Limited, Charham, chairman; Carl Crober, Dow Chemical Company, Sarnia,

Kuster   Russell

vice-chairman; G. I. Russell, G. I. Russell and Company, Limited, Burlington, secretary-treasurer. The Southern Ontario Committee on Electrolysis was formed on June 21, 1951. Currently more than 40 companies are represented. It is made up of a general committee, a western technical committee and a central technical committee.

The general committee is the governing body, while the two technical committees handle all corrosion cases presented to the organization and recommend tests necessary, analyze data obtained from tests and make a complete report to the general committee.

Currently the technical committees have more than 20 active cases on file and numerous other cases have been closed to the mutual satisfaction of all parties. The committee acts as an information center for any company requesting information on the location of underground plant. Advice is given to companies who do not have a regular testing program. Cases handled by the committee are principally of the cathodic interference type.

Western New York Committee Affiliates

Western New York State Corrosion Committee has affiliated with T-7A. Present officers are: E. K. Benson, chairman, New York Telephone Company, Buffalo, New York; R. L. Seifert, vice-chairman, Tennessee Gas Transmission Co., Hamburg, New York; E. L. Varney, secretary, Iroquois Gas Corporation, Buffalo, New York.

In August, 1956, sixteen underground

structure owners held a meeting in Buffalo, New York, to discuss the possibility of organizing a Corrosion Coordinating Committee in the Western New York State Area. C. A. Erickson, then chairman of the Western Pennsylvania Corrosion Committee, explained the operation of his committee and what the Western New York underground structure owners could expect to gain by the formation and operation of an active Corrosion Committee. After discussion it was decided unanimously that a committee should be formed. J. M. Fouts, then with New York Telephone Company, now with Koppers Co., Inc., was appointed temporary chairman.

First meeting of the Western New York State Corrosion Committee was held in Buffalo on October 31, 1956, with E. L. Varney, Iroquois Gas Corp. appointed secretary. At this meeting the committee by-laws were adopted. In March, 1957, Mr. Fouts resigned as chairman and E. K. Benson, New York Telephone Company, was elected to fill his unexpired term.

There now are 26 member companies represented on the committee.

Meetings are held on fourth Thursdays monthly in different cities in the operating area of the committee which is all of that part of New York State w/o route #11 connecting Binghampton, Courtland, Syracuse and Watertown. All companies or municipalities owning underground plant in this area are welcome to become members.

The committee has considered 17 corrosion coordinating cases to date.

Work is progressing toward the completion of a personnel directory, underground structure directory and a rectifier and bond directory.

Electrolysis Committee of Southern California Joins

The Electrolysis Committee of Southern California has affiliated with T-7, Corrosion Coordinating Committee under Unit Committee T-7E, Western Region Corrosion Coordinating Committee.

Officers of the Electrolysis Committee are: I. C. Dietze, Department of Water and Power, City of Los Angeles, Los Angeles, Chairman; F. F. Knapp, Vista, secretary.

San Diego Underground Committee Added to T-7

The San Diego County Underground Corrosion Committee has affiliated with the NACE Technical Group T-7, Corrosion Coordinating Committee under Unit Committee T-7E, Western Region Corrosion Coordinating Committee.

Officers of this committee are: W. M. Schilling, Southern Counties Gas Company, Los Angeles, chairman; R. Ditto, California Water and Telephone Company, Chula Vista, vice-chairman; F. O. Waters, City of San Diego Water Department, San Diego, secretary.

Task Groups Added To Cathodic Protection Criteria Committee

Unit Committee T-2C, Minimum Current Requirements for Cathodic Protection has requested that its name be changed to "Criteria for Cathodic Protection."

R. M. Wainwright, Good-All Electric Manufacturing Company, Ogallala, Nebraska, chairman of T-2C has announced the formation of the following task groups:

T-2C-1—To examine basic criteria that can be used for determining the adequacy of cathodic protection; also to study the possible consequences of over-protection. Chairman: Frances Ringer, Narberth, Pa.

T-2C-2—Examine coupons as a criteria for cathodic protection. Chairman: H. J. Keeling, Los Angeles, Cal.

T-2C-3—Survey and assemble present practices of operating organizations and engineers and their criteria for cathodic protection. Chairman: Robert Pope, Quakertown, Pa.

T-2C-4—To promote research and technical papers on criteria for cathodic protection. Chairman: L. P. Sudrabin, Electro Rust-Proofing Corp., Belleville, New Jersey.

Sea Water to Be Made

Cathodic protection tests on a series of panels in stagnant synthetic sea water made up by one of the commonly recommended formulations has been discussed by T-2C. On two bare coupons rust spots were encountered in spite of potentials greater than the —0.85 V normally sufficient to produce protection. Over the protected surface a uniform potential of —1.06 to a copper-copper sulfate cell was observed, but over rust spots variable readings were obtained ranging from 1.00 to 1.3 volts. After sand blasting and placing back into the system, rusting occured at the same spots. Potentials were measured by a salt-bridge probe ½ mm in diameter located within 1 mm of the surface and there was no detectable difference between readings with a Miller meter and a vacuum tube voltmeter.

A circumstance was reported in which a potential of around one volt was observed without reaching protection. It was a condenser installation with an 8-pound iron anode carrying one ampere impressed current. The anode lasted only two weeks. When the condenser was shut down, a voltage of 1.0 or better was measured with no indication of polarization. An independent iron specimen buried in earth essentially free of oxygen, showed a potential of —0.85 volt.

A member of T-2C has suggested that at any time leaks are found in areas where potentials more negative than —0.85 are measured by normal cell location, further exploration should be

Some Results of Inhibitors' Use in Product Pipe Lines Reported to T-2E Committee

Dillon Is New T-5 Vice-Chairman

C. P. Dillon, Union Carbide Chemicals Company, Texas City, Texas, has been elected vice-chairman of Group Committee T-5 on Corrosion Problems in the Process Industries. Mr. Dillon also is chairman of Unit Committee T-5A on Corrosion Problems in the Chemical Manufacturing Industry and Task Group T-5C-1 on Corrosion by Cooling Waters, South Central Region.

New Telephone Number
CENTRAL OFFICE NACE
is
CApitol 4-6108

Data on three sets of in-line corrosion coupons from pipe line exposure tests have been reported to Unit Committee T-2E on Internal Corrosion of Products Pipe Lines and Tanks. In a discussion of internal corrosion it was pointed out that corrosion seems to be more severe at origin points than at intermediate and terminal points. It appears there may be a decrease in oxygen content as products move through the lines because corrosion products seem to change from red to black as the distance from input point increases.

One member mentioned that some moisture appears to be necessary to build up a protective film with their organic inhibitor in use.

A products line which was in service seventeen years without inhibitor has been described to the committee. Some sections of the line were perforated from internal corrosion and had to be replaced. Application of inhibitor resulted in good clean-up of remaining line.

It was reported that some cone tanks at ocean terminals averaged 20 mils per year corrosion in the area 60 to 80 percent above bottom.

Two members said they had noted a marked decrease in scale collected on top of floating roof tanks where inhibited gasoline was stored.

A member reported that severe bottom corrosion had been experienced in the peripheral area of a flat-bottomed tractor fuel tank.

Another member reported that one company has computed corrosion loss on tankage at approximately $8000 per year on a 90,000-barrel aviation gasoline tank.

The idea was expressed that storage tank corrosion has increased in severity in recent years. Some feel that this is due to reduction in gum-forming constituents. Another idea expressed was that corrosion of cone roof tanks might be controlled by installing dehumidifiers on the vents to keep moist air out of the products.

A questionnaire to obtain data on existing corrosion in storage tanks was decided upon. Dr. Ivy M. Parker, Plantation Pipe Line Company, Atlanta, Georgia, chairman of T-2E reported this questionnaire will be a principal item of discussion at the fall meeting of the committee at the Northeast Regional Meeting in Pittsburgh, November 12-14, 1957.

E. P. Teale

E. P. Teale, American Telephone and Telegraph Company, Washington, D. C., died July 31. He had been vice-chairman of Group Committee T-4 on Utilities since March of this year and had served on several of the utilities unit committees for several years.

He was educated at John Hopkins University, Baltimore, Maryland, where he majored in electrical engineering. He engaged in numerous phases of communication outside plant engineering and maintenance work since 1918, chiefly corrosion control and inductive coordination problems. He had been a member of NACE since 1948 and was also a member of AIEE.

nother Wrought Iron case against corrosion

Photomicrograph T-90-2 (100x) shows a typical area—parallel to rolling—of the microstructure observed in the subject 10-inch wrought iron pipe.

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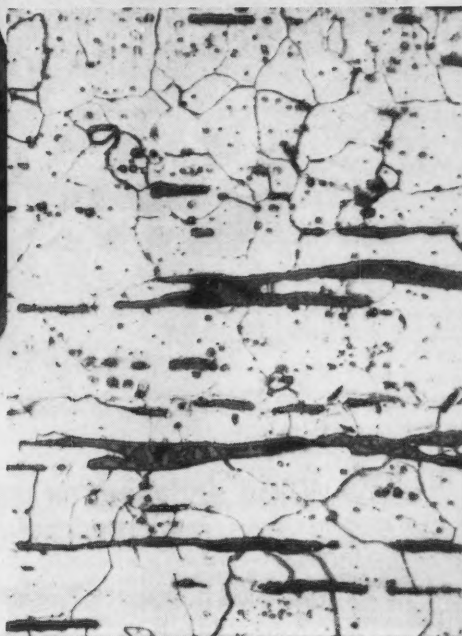
Metallurgical Report 5460—Fire Protection Line*

This report deals with the metallurgical examination of a length of 10-inch wrought iron pipe, submitted to our laboratory for investigation and comment.

The sample submitted had been in service for over 50 years as a fire protection line, yet proved to be in excellent condition. Both the outer and inner surfaces showed no evidence of localized pitting. No thinning of the pipe wall was observed. The inner surface was covered with a uniform layer of rust tightly adherent to the metal.

ROCKWELL HARDNESS

A cross-sectional ring was prepared for hardness determination. Hardness values taken around the cross-sectional ring indicated a B66 hardness, typical for wrought iron pipe, and showed that the strength and ductility were likewise normal.

CHEMICAL ANALYSIS

Carbon—.018%; Manganese—.036%; Phosphorous —.130%; Sulphur—.016%; Silicon—.150%; Iron Silicate—3.59%.

SUMMARY

Results of the laboratory examination serve as positive identification of the subject sample as wrought iron. Significant is the fact that this sample has successfully withstood corrosive attack for more than fifty years. This is the kind of documentary evidence which has earned wrought iron such an outstanding reputation in corrosion control. A. M. Byers Company, Clark Building, Pittsburgh 22, Pa.

* Name of actual installation given on request.

Write for free cloth-bound book, *Wrought Iron: Its Manufacture, Characteristics and Applications.*

BYERS
WROUGHT IRON

Task Groups Added—

made. Steps should be taken to determine if there is a local cell present not equal to the 0.85 volt criterion, but too small to be located by normal techniques.

Two Methods Are Used

Some members believe it is better to work to a value that will get enough protection to be economically feasible as the basic determination and build up toward more complete protection from that point than to use the —0.85 volt value as a criterion of protection. One member reported successful results on 300 feet of bare steel pipe by using a criterion of lowering the pipe-to-soil potential by 0.3 volts. The —0.85 volt figure has been proved a good figure for many installations, while the use of the criterion of lowering the potential has been good in others.

A member has reported that a series of lead coupons with cathodic protection were polarized to various values running from an unprotected blank to 1.5 volt potential with the higher potential having 30 to 35 ma current. After 20 months' burial the tests showed that sulfate reducing bacteria had acted on the specimens, with greatest activity on the coupon with highest polarization. It was postulated that the hydrogen polarization drove away oxygen and gave the bacteria an oxygen-free atmosphere in which to grow.

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Corrosion publishes annually in December an alphabetical subject index to its Technical Section.

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NACE NEWS

Key Biscayne, Pittsburgh Meetings Scheduled

W. H. Stewart to Be Boston Section's December 12 Guest

Plans for the season's programs were discussed by George Hunt, Simplex Wire and Cable Co., Cambridge, Mass. at the Greater Boston Section meeting held September 18. Members were asked by Wayne H. Keller to support and attend the Northeast Region "Golden Triangle" meeting, Pittsburgh, Pa., November 12-14.

W. H. Stewart, Sun Pipe Line Co., president of NACE will be a guest at the section meeting on December 12 when a reception will be held in his honor. Technical speaker will be H. H. Uhlig, Corrosion Laboratory, Massachusetts Institute of Technology. His topic will be "Corrosion Case Histories."

Other programs planned are: January 22—Local Corrosion Problems, a panel discussion by Elliot R. Perkins, New England Telephone and Telegraph Co.; J. E. O'Neil, Metropolitan Transit Authority; D. J. Allia, New England Power Service Co. Corrosion of Germanium by Harry C. Gatos, Lincoln Laboratory, Massachusetts Institute of Technology. Meeting to be held jointly with The Electrochemical Society at the Watertown Arsenal.

May 21—Spray Coating Metals by Harvey S. Miller, New England Hard Facing Co., Inc.

At the September meeting, A. G. Sternberg, technical director Steelcote Manufacturing Co., spoke on epoxy coatings. He discussed five classes of epoxy coatings: Epoxy esters, air-dried materials resembling phenolics, epoxy amines, common two-package compounds; epoxy ureas, similar to the amines but slower curing; epoxy phenolics, among the most useful of which are baked coatings and coal-tar epoxies.

He said epoxy polyamides are recommended for simplicity of mixing and application and wide tolerances in application techniques. He pointed out other characteristics of the coating: High solids in the liquid mass, fast buildup, applicability with conventional spray equipment and good exothermic properties. Outstanding values of the cured film include strength, resistance to abrasion, strong adhesion to many materials including especially concrete, ease of repair, usefulness for special purposes when filled with such metals as iron and copper.

For immersion service, Mr. Sternberg recommended the use of a zinc-filled primer on steel to provide cathodic protection and offset the hazard of hydrogen blisters from penetration of the film by water and attack on the steel. A lively question period followed the talk.

A door prize was won by Miss Marie Volk, a member and S. Lewis Doughty of Waterbury, a guest.

SECTION CALENDAR

Nov.
5   Shreveport Section. Caddo Hotel.
6   Metropolitan New York Section. Chi-Am Chateau, Route 22, Westfield, N.J. K. G. Compton, Bell Telephone Laboratories: Atmospheric Corrosion: Contributing Factors, Experience and Testing Techniques.
19 Chicago Section. Field Evaluation of Pipeline Coatings, M. E. Parker, Consulting Engineer, Houston.
19 Cleveland Section. L. West, Pipe Line Div., Standard Oil Co., Cleveland.
25 New Orleans-Baton Rouge Section. Engineers Club, DeSoto Hotel, New Orleans. Hal Hynes, Mavor-Kelly Co., Houston.
26 Southwestern Ohio Section. Chemical Corrosion, sponsored by National Distilleries. At Cincinnati.

Dec.
3   Shreveport Section. Washington-Youree Hotel, Shreveport.
11 Metropolitan New York Section. Chi-Am Chateau, Westfield, N.J. Special Christmas Meeting. NACE corporate memberships; W. H. Stewart, Sun Pipe Line Co., Beaumont, special guest.
17 Philadelphia Section. Poor Richard Club, M. G. Fontana, Ohio State University, Columbus: Various Approaches to Corrosion Problems.
17 Southwestern Ohio Section. Christmas Party.
17 Cleveland Section. Anton de S Brasunas, American Society for Metals.
30 New Orleans-Baton Rouge Section. Engineers Club, DeSoto Hotel, New Orleans.

All section meetings are held at the Beaconsfield Hotel, Brookline, Mass. except the March 4 meeting at Watertown Arsenal. Meetings start at 5:30 p.m. with a social hour followed by dinner at 6:30. A brief business meeting and the technical meeting follow, starting at 8.

Salt Lake Section Plans Corrosion Show

A corrosion show is scheduled to be held at the Newhouse Hotel, Salt Lake City November 19 by Salt Lake Section.

The section's October 22 meeting program included a visit to the Geneva Steel Co., Provo, Utah. On September 24 Bert Espiau, Pipe Linings, Inc., Wilmington, Cal. spoke on internal coatings for pipelines and discussed synthetic coatings generally. Members convened at the Fisher Brewery, which was toured prior to the technical program.

Illinois University Cathodic Protection Course Also Planned

Two more multiple-day meetings are scheduled to be held during November to bring to a close the flurry of activity that has characterized the months of September, October and November for NACE. These two will be:

November 12-16—A combined technical conference and short course at Key Biscayne, Fla. sponsored by Miami Section.

November 12-14—The Golden Triangle meeting of Northeast Region at Hotel Penn-Sheraton, Pittsburgh.

Details of these meetings were published in October CORROSION as follows: Key Biscayne, Page 99; Pittsburgh, Page 104.

Before the Christmas hiatus a short course on cathodic protection will be held at University of Illinois. Details of this biennial event were published in June CORROSION beginning on Page 98.

A short course will be held at Hotel Mayo, Tulsa, February 12-14 sponsored by Tulsa Section. This is the section's ninth annual course for pipeliners.

Houston Section plans to hold a short course shortly after the first of the year but dates have not been announced.

Tanker Corrosion Project Discussed at New York

Cathodic protection, inhibitors and coatings being tested cooperatively in the American Petroleum Institute's Tanker Corrosion Research Project were described October 4 at a meeting of Metropolitan New York Section. Donald M. McLean, assistant project coordinator was the speaker.

Four members of a symposium on coatings covered a wide range of information at the September 11 meeting of Metropolitan New York Section. The symposium, titled "Common Conventional Coatings for Corrosion Prevention of Underground Structures," was presented by F. J. Kiernan, Barrett Division, Allied Chemical & Dye Corp., moderator; Frank Koeffler, Pittsburgh Coke & Chemical Co.; V. C. Robinson, Dearborn Chemical Co. and George Roberts, Polychem Div., Kendall Co.

Included in the discussion were data relating to specifications and procedures, coal tar base materials, asphalt, microcrystalline waxes and plastic tapes.

There were 64 members and 18 guests present.

Alamo Section Meets

The September 17 meeting of Alamo Section featured a smoker and a brief business session at the cafeteria of the Telephone Building in San Antonio.

North Central Region Will Meet in Cincinnati

The 1958 meeting of North Central Region has been scheduled for October 15-17 at Hotel Sheraton-Gibson, Cincinnati. Southwestern Ohio Section will host.

Research on Fire Paying Dividends Now
Standard Oil Researcher Tells Chicago

If You Were Misled, This Is R. B. Mears

In Case anyone was mislead by the error on Page 104, October CORROSION where a photograph was incorrectly identified as that of R. B. Mears, a recent photograph is reproduced here. Dr. Mears, who is in the Applied Research Laboratory, U. S. Steel Corp., Monroeville, Pa. will present a paper on electrochemical measurements during the Pittsburgh Golden Triangle meeting.

Mears

Besides being one of the early (1945) members of NACE, Dr. Mears has a worldwide reputation for his accomplishments and writings on fundamental corrosion phenomena and is well known personally and by repute to hundreds of NACE members. He was NACE president in 1949-50 and received the 1949 Willis Rodney Whitney Award.

R. V. Moorman Is Elected By Portland, Ore. Section

R. V. Moorman, Bonneville Power Adm., Portland is new chairman of Puget Sound Section. Also named were John Van Bladern, Portland Gas & Coke Co., 132 N.W. Flanders, St., Portland, vice-chairman and William R. Barber, Jr., Electric Steel Foundry Co., Portland, secretary-treasurer.

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More than 10,000 NACE Corrosion Abstract Cards have been published so far.

Research into fire, the oldest chemical reaction used by man, is paying dividends, according to James A. Bowman, Standard Oil Co., research laboratories, Whiting, Ind. Scientific findings have made it possible to get the work of three gallons of gasoline of the kind made in 1925 by using only two gallons made by modern methods, he said.

Mr. Bowman demonstrated complex research findings on fire to 81 members and guests attending the NACE Chicago Section meeting, September 17 at the Chicago Engineers' Club.

Gas filled soap bubbles were used to demonstrate how widely fuels may be made to vary in their burning. Filled with hydrogen alone, the bubbles burned lazily. With oxygen added, burning was so violent the explosion shook the windows. Use of a catalyst to promote burning was demonstrated. A lump of pure sugar could not be ignited by ordinary means, but when cigarette ashes were added, the sugar burned readily. Invisible pictures which suddenly burst into flames, a bright fire created with only a handful of iron wire as fuel and other unusual experiments were conducted by Mr. Bowman.

"Fire is a high-temperature reaction and so is hard to control. In our research we are interested principally in the small fires you build by the thousands everyday—the fires in the cylinders of your automobile. When you are driving 40 miles an hour, you are building more than 100 of these fires every second. And they have to be just the right kind or your car doesn't run right," Mr. Bowman concluded.

Because of the North Central Region meeting, no plans were made for a Chicago Section meeting in October. V. M. Kalhauge, Standard Oil Company of Indiana, section chairman introduced officers and committee chairman. A change has been made in sponsorship of the fellowship hours. Instead of a single firm or group sponsoring each meeting, all sponsors will combine to take care of all meetings.

Hustead Succeeds Happel As East Texas Chairman

B. G. Hustead, East Texas Salt Water Disposal Co., Kilgore, Tex., is the new chairman of East Texas Section replacing P. E. Happel, Sun Oil Co. who has been transferred to Crystal City, Miss.

Nomination of a slate of officers for 1958 is in progress under the direction of Gene E. Smith, Lone Star Steel Co., nominating committee chairman.

Scheduled for the October 22 Section meeting was a talk on "Corrosion in the East Texas Field" by Harry G. Byars, Atlantic Refining Co., Dallas.

At the September 24 meeting in Longview section members and guests saw a sound-color film of the Tidewater Oil Co. new Delaware refinery. On the lighter side, they also enjoyed "High Lights of 1956 Football," a color movie produced by Humble Oil and Refining Co. Fifteen members and 31 guests attended.

The section meets the fourth Tuesday monthly.

Two Starts to a Better Finish...
at Lower Cost

HOT SPRAY makes use of controlled heat to maintain constant paint viscosity. The results—better finish, shorter drying time, improved coverage and flow-out and sizeable savings in materials—are widely recognized in maintenance painting.

ALL THESE ADVANTAGES are now offered in two new Spee-Flo hot spray units specially designed to provide the portability and long hose lengths needed for maintenance painting. Completely self-contained, these new units combine the famous Spee-Flo hot spray heater and divorced action reciprocating pump in models which carry the original five or fifty-five gallon paint drum.

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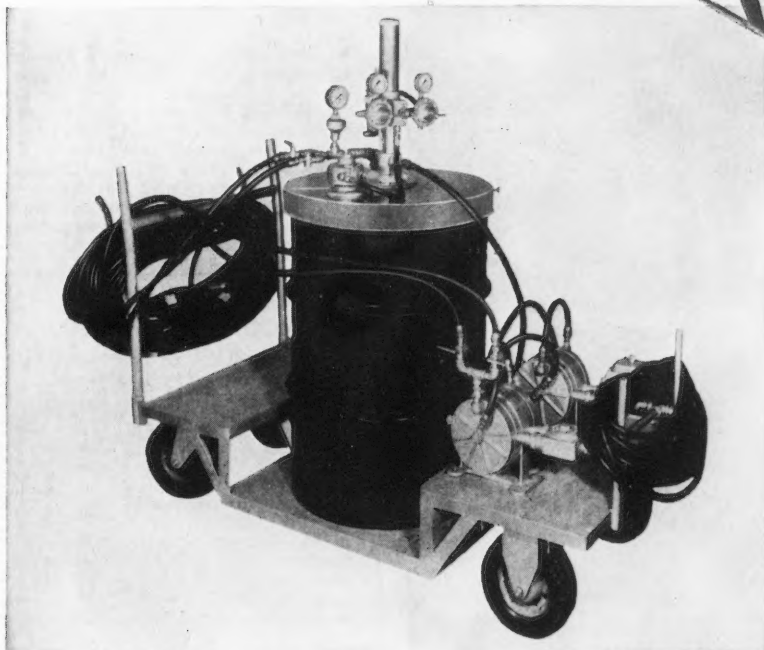
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Golden Triangle Ready for Influx Of NACE Members

Everything is ready for the November 12-14 Northeast Region meeting in the "Golden Triangle." The program of 19 technical papers and demonstration, and 11 technical committee meetings has been complete for some time. A resume of this portion of the program was published in October CORROSION beginning on Page 104. All events are at Hotel Penn-Sheraton, Pittsburgh.

A list of the eight industry tours offered and a brief summary of what is to be seen on each was published in October CORROSION on Page 110. Photographs of three tours are in adjacent columns.

In addition to previously announced entertainment the following have been added to the program:

The Westinghouse Quartet will entertain during the November 13 annual banquet. This group, which has been singing 26 years is made up of Walter X. Eibeck, first tenor; Alvin F. Headrick, second tenor; Robert C. Howes, baritone and John K. Power, bass. Despite more than 6000 appearances at concerts, banquets, club meetings, hospitals and other programs, members of the quartet hold down full time jobs and singing remains a hobby. Mr. Howes and Mr. Power joined the group this year, becoming the 13th and 14th personnel changes since it was organized in 1931.

Charles LeRoy, internationally famous amateur astronomer, will be the featured speaker at the banquet. Current interest in the subject will make his remarks about satellites even more interesting than would be the case otherwise.

Ladies are assured of an additional treat in an opportunity to see new gowns created entirely from aluminum by Alcoa. The gowns will be modeled throughout the dinner hour.

BACK ISSUES OF CORROSION OFFERED

A rare opportunity has been offered by S. W. Green, 3310 West 66th St., Los Angeles, Cal. to some person interested in securing complete files of CORROSION for years 1952-56 inclusive. Any person or firm interested in securing these back issue copies is invited to write to him concerning them.

NACE central office is unable to supply complete files for these years and the opportunity to get them is extremely rare.

SCENES AT THREE of the eight industrial plants to which tours will be offered November 13 during the Northeast Region's Golden Triangle Meeting at Pittsburgh are, top to bottom: Gulf Research and Development Laboratories, Harmarville; a 4000-ton extrusion press at Aluminum Company of America's New Kensington, Pa. works and U. S. Steel Corp. Research Center, Monroeville, Pa. The Edgar C. Bain Fundamental Research Laboratory is on the left and the Applied Research Laboratory on the right. A list of the eight tours offered was published on Page 110, October CORROSION.
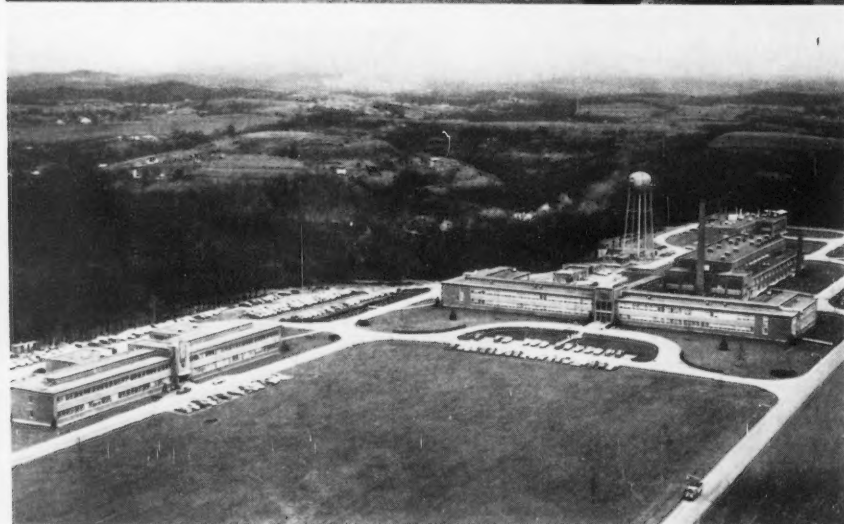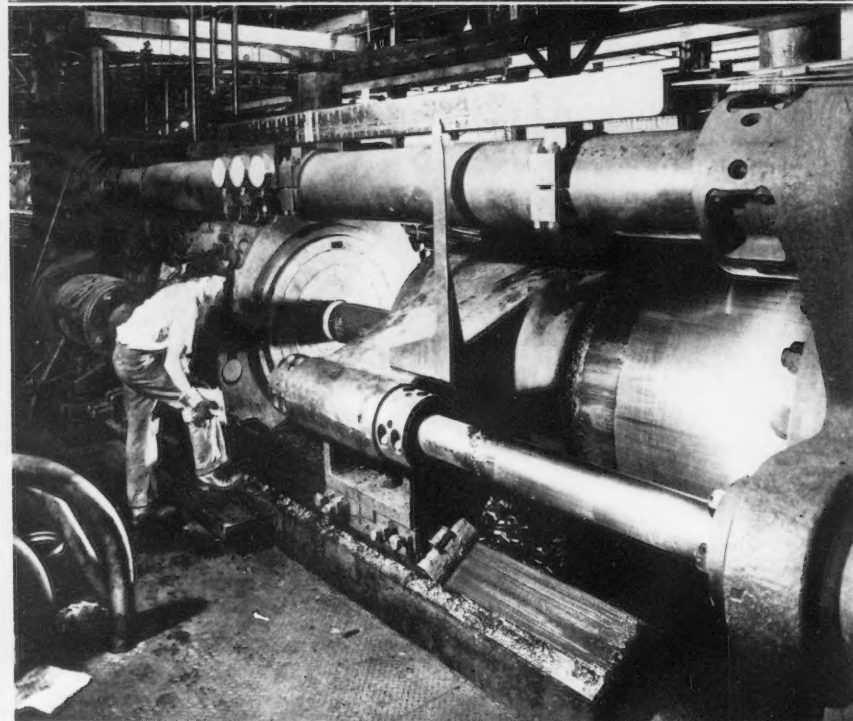
NACE aims to use CORROSION as a medium for coordinating corrosion control work the world over.

A list of available reprint copies of technical reports and articles from CORROSION is available on request.

Kansas City Section's Activity to Increase

National activities of NACE as they concern the Kansas City Section shared attention with local section activities at the September 9 meeting at the Wishbone restaurant.

Bob Malley, Deady Chemical Co., Kansas City, Kas., section chairman, announced that the 1962 national NACE Conference and Exhibition will be held in Kansas City, Mo. with meetings and exhibits at the municipal auditorium. Another national project in which the section hopes to be prominent is the drive for corporate memberships. Mr. Malley told the group a chairman will probably be appointed to handle this activity.

Principal local activities were the selection of a nominating committee, a campaign to obtain more members and a discussion of possible sources of technical programs for future meetings.

The nominating committee consists of Jack Grady, Corrosion Control Co., chairman and Robert Hancox, Great Lakes Pipe Line Co.; John Berringer, Panhandle Eastern Pipe Line Co. and Lon Neal, Black, Sivalls & Bryson, Inc.

Firms discussed as possible sources of programs and the subjects they could provide for future meetings were: Marley Company, wood preservation; Black & Veatch, waterside corrosion; Spencer Chemical Co., polyethylene; Standard Oil Co., corrosion inhibitors and Deady Chemical Co., cooling tower corrosion.

Mr. Grady said section membership was 79. Dick Fuller, membership chairman reported that since the May meeting, approximately 50 letters had been sent to prospective members.

Following the business meeting a film, "Voice Beneath the Sea" was presented by L. D. Weiser, Southwestern Bell Telephone Co., Topeka, Kans.

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More than 10,000 NACE Corrosion Abstract Cards have been published so far.

1958 Abstract Card Subscriptions Solicited

New and renewal subscriptions to the Corrosion Abstract Punch Card Service of National Association of Corrosion Engineers will be accepted until January 15. The 1958 subscription price, $100 for domestic subscribers, is estimated to include about 2100 cards.

The NACE punch card service consists of 5 x 8-inch double row perimeter punched cards on which abstracts of corrosion literature are printed and coded for topic, reference date and first and last author. Cross-indexed topics are pre-punched for a maximum of four topics, the other references are marked for punching by non-technical assistants. Additional blank cards are available for multiple filing or coding. Unused holes are provided for supplementary indexing and cards are serially numbered for integration with automatic sorting systems.

At the end of 1957 the punch card service will have issued 14,699 references. Back issue subscriptions are available for 1951, 52, 53, 55, 56 and 57 in limited numbers. Firms interested in securing this outstanding research tool are invited to address inquiries to Central Office.

Tulsa Section Arranges Six More Meetings

Six more meetings beginning with one scheduled November 25 will be held by Tulsa Section at Mayo Hotel Tulsa during the current section year. A schedule listing meeting dates for January 27, February 24, March 24, April 28 and May 26 has been made, but no program announcements were available.

Meetings have been held also in September when Tom Wilkinson spoke on "Latest Developments in Rectifiers for Cathodic Protection," and on October 28 when T. Roger Betty, E. I. duPont de Nemours & Co., Inc., conducted a clinic on maintenance uses of Teflon.

Bruce Replaces Cloud On Abstract Subcommittee

G. H. Bruce, for the past year engaged in technical research work in the Houston Research Library of Humble Oil & Refining Co. is new member of the Abstract Subcommittee of the NACE Publication Committee. Mr. Bruce, who was research engineer with Humble's Production Department for eight years, engaged in inquiries concerning drilling muds, reservoir behavior, separation of oil and gas and other problems, is a member of NACE and of the Society of Petroleum Engineers of AIME.

Bruce

He also is a member of the local section of American Petroleum Institute. He has a BS in physics (1949) University of Texas. He replaces Dr. Gould H. Cloud, Carter Oil Co., Tulsa.

NATIONAL and REGIONAL MEETINGS and SHORT COURSES

1957

Nov. 12-14—Northeast Region Fall meeting, Pittsburgh, Pa., Penn-Sheraton Hotel.

1958

Mar. 17-21—NACE Annual Conference, Civic Auditorium, San Francisco, California.

Oct. 5-8—Northeast Region, Somerset Hotel, Boston, Mass.

Oct. 15-17—North Central Region. Cincinnati, Ohio.

Oct. 20-24—South Central Region. New Orleans, Roosevelt Hotel.

1959

NACE Annual Conference, Sherman Hotel, Chicago, Illinois.

Oct. 12-15—South Central Region Meeting, Denver, Col.

SHORT COURSES 1957

November 12-15—Miami Section Short Course, Key Biscayne, Fla.

December 9-13—Biennial Short Course on Cathodic Protection. University of Illinois and NACE.

SHORT COURSES 1958

Feb. 12-14—Ninth Annual Tulsa Corrosion Short Course for Pipeliners, Mayo Hotel, Tulsa, Okla.

Tulsa Short Course Set

The Ninth Annual Tulsa Corrosion Short Course for Pipeliners will be held February 12-14 at the Mayo Hotel, Tulsa. Robert M. Nee, The R. M. Nee Co., Box 3436, Whittier Station, Tulsa is general chairman.

Technical Program Is Oklahoma City Highlight

AT OKLAHOMA CITY October 3 at the Skirvin Towers Hotel this capacity crowd was present to participate in the South Central Region's annual business luncheon. Top photograph shows Dr. Kenneth McFarland, Educational Consultant to General Motors, guest luncheon speaker, who kept his audience in gales of laughter. Next, left, W. R. Scott, Jr., Crest Instrument Co., Santa Fe Springs, Cal. gives his paper "Some Recent Developments in the Application of the Electrical Resistance Method to Corrosion Studies." In the photograph to the right, F. W. Gartner, Jr., F. W. Gartner Co., Houston presents his paper "You Show Us How—We'll Do It." At bottom left, Dr. H. H. Bliss, University of Oklahoma, Norman tells how the $200 given to him for use in promoting Oklahoma Science Fairs among young people will be used. At the right, a tense moment in the presentation of the skit: "Mr. Corrosion Engineer—This Is Your Life," is shown as Bob Suman, Pittsburgh Plate Glass Co., Paint Div., Houston, as the "Squid Oil Paint" salesman asks Corrosion Engineer Charlie Nathan, Texas Company, Production Research Laboratory, Bellaire, Texas, "Who ever heard of a rusty squid?" Seated at the left is Miss Jackie Bowman, portraying the disheveled phase of "Miss Copyright," Nathan's secretary.

Exhibition Presents Oilfield Equipment And Many Materials

In several important respects, the October 1-4 meeting of South Central Region at Oklahoma City was considered outstanding by many. Attendance at and attention during technical committee meetings was exceptionally good, technical symposia were well-patronized; and most registrants took time to visit the exhibition and view the 35 displays presented.

Total registration was in excess of 600. This is considered to be an exceptionally good showing for a meeting held at the northwest corner of the region.

If any feature of the meeting could be singled out as outstanding, it was the region's educational committee booth at the exhibition. This booth attracted consistent and favorable attention by many visitors. Principal focus of interest was the Corrosion Control Demonstration engineered and developed by young Stephen H. Caine, Shreveport, La.

Exhibits in Oil Field

Almost all of the exhibits were oriented to the petroleum business, as would be expected from the location of the show and the interests of the persons at the meeting. Several firms new to NACE exhibitions were in the show for the first time.

In spite of this concentration on the petroleum industry, there was a wide variety of materials and equipment on display. Included were instruments, pumps, numerous kinds of coatings and tapes, insulators, spacers, cables, rectifiers, inhibitors, metal and plastic tubing, wrapping, holiday detectors and other items.

Good Attendance Noted

Attendance at the annual business luncheon was exceptionally good, perhaps better than that at any previous like meeting. This was an aim of the region in setting the luncheon earlier in the program and arranging for a featured speaker.

Attendance at the annual banquet was good—almost a capacity crowd—evidencing the wisdom of offering a "package deal" registration. The entertainment was vastly appreciated, consisting of local talent in a skit originated by Joe E. Rench, Napko Corp., Houston.

Dancing, although late in starting because the orchestra did not arrive on time, was enjoyed by a large number.

A varied ladies' program was provided including a luncheon, style show and other events.

Cleveland Section Tours Sherwin-Williams Plant

Cleveland Section members were conducted on a tour of the Sherwin-Williams plant for the September 17 meeting. M. W. Hurdelbrink, Sherwin-Williams Co., addressed the group. A certificate was awarded to Al Hose, The Lindsay Wire Weaving Co., Cleveland, Ohio, past chairman. Dinner was served after the field trip to 40 members and 27 guests.

SOUTH CENTRAL REGION'S Educational Committee brought several recent activities to the attention of the region's members at the October regional exhibition at Oklahoma City's municipal auditorium. Shown are, top to bottom: Stephen H. Caine, Shreveport, Louis'ana high school boy and his "Corrosion Control Demonstrator." This device was developed for a science fair competition and brought young Caine a $150 award from the region at the annual business luncheon October 3. He conceived the device, which is automated and has its own coordinated taped commentary, as useful in instructing field personnel in corrosion fundamentals. Central photograph shows the "Corrosion Demonstration Kit" assembled by Houston corrosion engineers to be used by high school science teachers in demonstrating fundamental corrosion processes. Bottom photograph shows, left, H. V. Beezley, United Gas Pipe Line Co., Shreveport, vice-chairman and John E. Loeffler, Thornhill-Craver Co., Houston, chairman of the region's education committee in the booth at the exhibition. It received numerous favorable comments from many visitors.

Educational Exhibit Focus of Attention At Oklahoma City

The South Central Region Educational Committee booth at Oklahoma City was interesting to hundreds and commended in general and in particular by many visitors. The idea for the booth, germinated among members of the committee headed by John E. Loeffler, Thornhill-Craver Co., Houston chairman, proved to be a worthwhile one.

The booth, located on the exhibit floor at the municipal auditorium, consisted of two principal items: The Corrosion Control Demonstrator developed by Stephen H. Caine, Shreveport, La., high school student and the Corrosion Demonstration Kit, developed by several corrosion engineers in the Houston area.

Demonstrator Fascinates

Young Caine's demonstrator consisted of a bank of specimens in a rack above a console including electrical instruments. Its operation was automatic and keyed to a commentary recorded by the builder of the kit. When activated the commentary started and as each fundamental of corrosion was explained, the appropriate specimen was lighted. Ammeters showed the electrical phenomena involved.

The kit, selected from among a number of science fair displays in the South Central Region area, was envisioned by the builder as a means of instructing field personnel in the fundamentals of corrosion. Caine, in addition to receiving the honor of having his demonstrator shown at Oklahoma City, received a gratuity of $150 from the region.

Demonstration Kit

The Corrosion Demonstration Kit, another project of the region's educational committee, was assembled by a number of corrosion engineers in the Houston area. It is intended to be given to teachers of high school science classes to be used in demonstrations of basic corrosion phenomena.

The committee contemplates giving kits to teachers in schools that show an interest in the science area related to corrosion reactions. It is believed that the use of this kit may develop an interest in young science students in continuing scientific careers generally and in corrosion engineering specifically.

The science kits were assembled by a task group of Houston Section headed by M. A. Riordan, Rio Engineering, chairman; C. L. Woody, United Gas Corp.; L. R. Sheppard; and Robert G. Ranson, Tennessee Gas Transmission Co. all of Houston.

M. B. Hart

M. B. Hart, Illinois Bell Telephone Company, Chicago, and a member of the National Association of Corrosion Engineers since May 15, 1945 died May 30. Mr. Hart, electrolysis engineer for his company for more than 18 years was an active participant in NACE affairs.

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The NACE Abstract Filing System is used by many organizations.

NORTH CENTRAL REGION'S Chicago meeting October 2-4 brought the panel of speakers shown in the top photograph to present five papers during the Protective Coatings Symposium. On the platform, left to right are: W. R. Brooks, Binks Mfg. Co.; J. H. Geyer, American Chemical Paint Co.; C. A. Van Natta, Plastic Linings Coatings, symposium chairman; L. W. Gleekman, Wyandotte Chemical Co.; F. J. Ploederl, Wisconsin Protective Coatings and, standing, F. J. Kiernan, Barrett Division, Allied Chemical & Dye Corp. The small photographs on the left show, top, T. E. Larson, Ilinois State Water Survey, and bottom, L. V. Sorg, Standard Oil Co. of Indiana, delivering papers in the Water Treating Symposium. At their right is the group participating in the Cathodic Protectoin Round Table discussion conducted by G. G. Wilson, Institute of Gas Technology. The bottom scene during the Fellowship hour shows, left to right, Harry J. Miller, Amercoat Corp., Evanston, Ill.; R. W. Flournoy, Reynolds Metals Co., Louisville, Ky. and W. E. Hare, Hare Equipment, Cincinnati.

"KARBATE" IMPERVIOUS GRAPHITE SHELL AND TUBE HEAT EXCHANGERS PROVE THEIR ECONOMY IN COOLING CORROSIVE GASES

Gas coolers of "Karbate" Impervious Graphite cost less and last longer than coolers made of less corrosion-resistant materials.
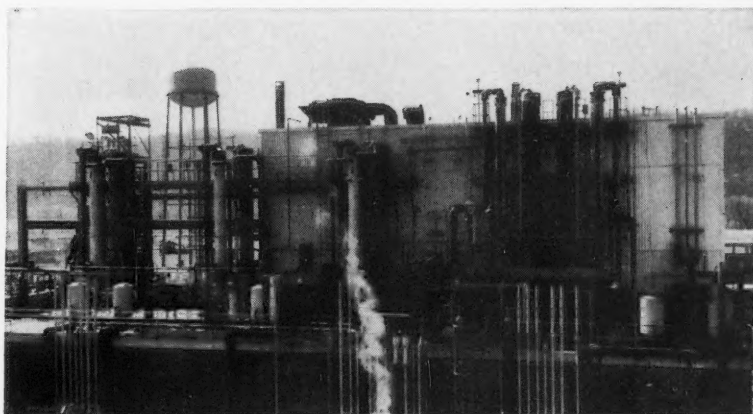
Ten "Karbate" Impervious Graphite Shell And Tube Heat Exchangers cooling and condensing mixtures of organic vapors and hydrogen chloride. Units are arranged in pairs—uninsulated unit in each pair has plant cooling water on shell side; insulated unit is refrigerated.
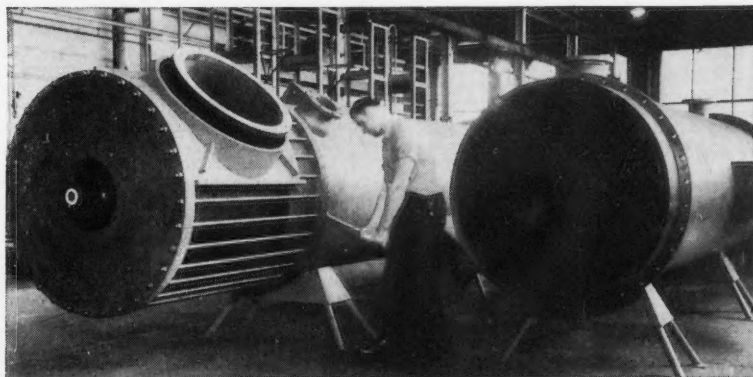
These standard "Karbate" heat exchangers have 685-⅞" I. D. "Karbate" tubes assembled between "Karbate" tube sheets in 45" diameter steel shells. Corrosive water-saturated sulfur dioxide gas, which contains considerable entrained sulfuric acid, will enter and leave tube sides through 24" diameter connections on "Haveg" phenolic resin covers.

National Carbon provides complete Technical Service—An experienced technical staff designs and rates "Karbate" Shell and Tube Heat Exchangers manufactured and guaranteed by National Carbon. Dr. D. Q. Kern, well-known consultant and author of PROCESS HEAT TRANSFER, serves as an advisor to this group.

Particularly significant today is the economical cooling of corrosive gases. "Karbate" Impervious Graphite Heat Exchangers have the corrosion resistance, high thermal conductivity, immunity to thermal shock, and moderate cost vital to this service.

For cooling corrosive gases, "Karbate" Exchangers operate either horizontally or vertically, usually with the corrosive gas inside the "Karbate" tubes and with the coolant in the steel shell. These exchangers are furnished with shells of "Haveg" phenolic resin, impervious graphite, rubber or glass-lined steel for operation with corrosive gas on the outside of the "Karbate" tubes.

A complete line of "Karbate" Heat Exchangers is available in sixteen shell sizes from 6" I.D. to 45" I.D. with tube lengths of 6', 9', 12', 14', and 16'. Standard components are carried in stock for immediate assembly of units having up to 3585 sq. ft. of heat transfer surface.

For full details, request **Catalog Section S-6800NL**

Shown here are the four members of a panel on "Corrosion in Water Distribution Systems" held at the San Francisco Section meeting Sept. 25. From left to right: H. J. Keeling, John M. Toups, V. L. Greedy and Lee Streicher.

Russian Definition of Engineer Affects Data On U.S. Numbers Disparity, Dreier Asserts

Alex Dreier, National Broadcasting Company newsman told those present at the North Central Region banquet in the Sherman Hotel Chicago October 3 that data on Russia's engineers is distorted by the fact the Russians tend to label as engineers anyone who has finished the equivalent of the tenth grade. Figures on graduates at the college level, he said, probably would show engineering graduates in Russia and the United States to be about equal in number. Mr. Dreier showed a color film of scenes taken during his recent visit to Russia.

The region's second annual meeting, held October 2-4 was conceded to have been a success in every respect, with registration totaling 270. Attendance at the technical symposia averaged 50 to 60. Round table discussions on cathodic protection and coatings were well received and attended.

Attendance of ladies was less than expected but the program arranged by Mdms. R. B. Janota, L. O. Risetter and Mark Fletcher was enjoyed.

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NACE Technical task groups are formed to reach limited objectives.

Scale to Be Topic of San Joaquin Section

"Scale: Causes and Prevention" is the technical subject scheduled for a meeting of the San Joaquin Section to be held the latter part of November.

The September 19 meeting was held in conjunction with NACE Technical Committee T-1A on Corrosion in Oil and Gas Well Equipment, Los Angeles Area at Maison Jaussaud restaurant, Bakersfield, Cal. Forty-four members and 20 guests attended.

For the technical program, three speakers formed a panel on cathodic protection. Fred Shremp, California Research Corp., La Habra, spoke on oil well casing. Richard Stark, Pacific Gas and Electric Co., Bakersfield, discussed pipe lines. Robert Davis, Superior Oil Co., Bakersfield, talked on cathodic protection of tanks. After the talks, the panel and audience participated in a question and answer session.

Water Distribution System Corrosion Is Topic of Panel

Corrosion in Water Distribution Systems was the subject of a panel discussion at the September 25 meeting of Los Angeles Section. Each panel member had a 15-minute presentation period. At the completion of the formal presentations, panelists answered questions from the floor.

Subjects discussed by panel members were: Corrosion Problems in Municipal Water Distribution Systems, by John M. Toups, district engineer, Orange County Water District; Corrosion Control Through Water Conditioning, by Lee Streicher, chief chemist, Metropolitan Water District of Southern California; In-Place Cement Mortar Recontioning, by V. L. Greedy, sales manager, Pipe Linings, Inc.; and Corrosion Control Through Cathodic Protection, by Harry J. Keeling, engineering consultant.

In addition to section members, nonmembers from water works groups in Southern California attended the meeting. It was estimated that of 122 persons present, 50 were guests, according to C. E. Hedborg, Union Oil Company of California, section vice-chairman.

For the benefit of the visitors, J. S. Dorsey, Southern California Gas Co., section chairman, gave a brief talk explaining the aims of National Association of Corrosion Engineers and recommended to visitors that they join NACE. The section membership chairman said many visitors requested application blanks after the meeting.

San Diego Section Kept Busy by Three Projects

Three separate but related projects have kept the San Diego Section quite busy: The Seventh Annual Western Region meeting, Oct. 23-25; conducting a night school on "basic corrosion" and holding the regular September section meeting.

A short report on the progress of arrangements for the regional meeting was given at the section meeting. Well

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SAN FRANCISCO's most noteworthy engineering achievement is the system of bridges spanning the passes between San Francisco Bay and the Pacific ocean. These bridges, in addition to being significant technical accomplishments also have the characteristic—frequently found in structures whose components have solely utilitarian functions—of unusual aesthetic appeal. In the view above, looking through the cables of the Golden Gate Bridge, the city is shown gleaming in the sun. While the curbside flower stall shown in the scene at the left is not spectacular, it illustrates another facet of the fascinating metropolis where the NACE 14th Annual Conference and Exhibition will be held. The large and small attractions that go to make up the appeal of San Francisco are too numerous to itemize, but they are sure to be magnets for association members and their wives next March.

Busiest Technical, Pleasantest Social Programs Arranged

Plans for the NACE 14th Annual Conference and Exhibition in San Francisco March 17-21 are rapidly approaching completion with indications the 1958 Conference will be one of the busiest technically and pleasantest socially in the history of NACE. Following is a summary of progress:

Technical Program

The Technical Program Committee,

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14th ANNUAL CONFERENCE
The Place   &   The Men   &   The Program

Little needs to be said about the appeal of San Francisco as a place to be and see. The illustrations on the facing page show two of these attractions—and a list of others equally interesting would be lengthy. Those who have been there welcome the chance to return while those who have not look forward to their first visit.

The conference committee is composed of men active in corrosion control on the Pacific Coast and in NACE affairs generally. They are making personal contributions of some magnitude to the success of the meeting by giving their time and energy.

It is not too soon to urge that those who plan to attend the NACE 14th Annual Conference and Exhibition next March to start making arrangements at once. The conference committee has arranged a technical program which it believes will be unequalled in variety and extent. The technical committees already have arranged for important discussions on most of the major problems of corrosion control. On the basis of the technical program alone the committee believes there is ample justification for a week's stay in San Francisco.

GENERAL CONFERENCE COMMITTEE
San Francisco, March 17-21, 1958

Publicity Committee: M. Garratt, Garratt-Callahan Co., 30 Rollins Road, Millbrae, Cal.

Ladies' Activities Chairman: J. Pappas, Electric Steel Foundry Co., 1280 Sixty-fifth St., Emeryville, Cal.

Technical Program Chairman
ELLIS D. VERINK
Aluminum Co. of America, New Kensington, Pa.

General Conference Chairman
D. R. LOPER
Standard Oil Co. of Cal., San Francisco, Cal.

Assistant General Chairman
G. J. PUCKETT
Dow Chemical Co., Pittsburg, Cal.

Technical Program Co-Chairman
R. McFARLAND
Hills-McCanna Co., Crystal Lake, Ill.

Transportation Chairman
JOHN R. CULVER
Coulter Steel & Forge, Emeryville, Cal.

Registration Chairman
P. J. RAIFSNIDER
Shell Development Corp., Emeryville, Cal.

Housing Chairman
L. HABBEN
Ryerson & Sons, Inc., Emeryville, Cal.

Entertainment Chairman
H. N. HARNER
Carpenter Steel Co., San Francisco, Cal.

Publicity Chairman
A. E. STORM
Tidewater Oil Co., Associated, Cal.

Exhibits Chairman
G. A. WORKS
Union Oil Co. of Cal., Rodeo, Cal.

Exhibits Committee
WILLIAM P. SIMMONS
Alloy Steel Products Co., San Francisco, Cal.

Exhibits Committee
ROBERT S. CAREY
Union Oil Co. of Cal., Rodeo, Cal.

Exhibits Committee
CHARLES M. SCHILLMOLLER
The International Nickel Co., Inc., Los Angeles, Cal.

Exhibits Committee
J. P. FRASER
Shell Development Corp., Emeryville, Cal.

Entertainment Co-Chairman
R. S. TRESEDER
Shell Development Corp., Emeryville, Cal.

Program Coordination Chairman
ROBERT L. PIEHL
Standard Oil Co. of Cal. Refinery, Richmond, Cal.

Busiest Technical—

headed by Ellis Verink of Aluminum Company of America, has completed the selection of authors and papers for the largest array of technical fare ever offered to the association. In addition to the symposia which have become traditional over the past years, three new ones will be added in San Francisco. These symposia, of special interest to people in the West, also willl appeal to many members of NACE across the entire country. They include a meeting on marine corrosion problems, a symposium meeting on corrosion problems in the pulp and paper industry and a symposium on the subject of corrosion of aircraft.

During the entire series of meetings in San Francisco, there will be three concurrent symposia from Monday afternoon through Friday morning, except Tuesday afternoon which is reserved for visiting exhibits.

In addition to the large and detailed symposia program, the technical committees will meet in greater numbers than ever before. Seventy tehcnical committee meetings are now planned.

Exhibits

Exhibits Chairman George Works of Union Oil Company of California advises that contracts were mailed to over 1000 prospective exhibitors in mid-August. Since the exhibit space in San Francisco Auditorium is limited, it is likely that it will be adaquately subscribed. Almost half of the available space has already been reserved and it is expected that the remainder will be filled soon. Among those who have responded to the initial opportunity for exhibiting in San Francisco area a number of the manufacturers who have over the years provided consistent support to the association and participated in previous exhibitions. Also, there are a num-

ber of new exhibitors, particularly representing Western industry.

Mr. Works' committee advises that they will have available comfortable and adequate facilities for all concerned. The Exhibit Hall will be located in the main arena of the San Francisco Civic Auditorium between the two principal meeting halls used for symposia.

The exhibit promises maximum convenience for people who wish to attend both technical meetings and the exhibit during the course of their conference day. The previous practice of opening exhibits at 9 am and running through Friday morning will be modified for the greater convenience of exhibitors and visitors alike. Exhibits will open at 10 am Tuesday through Thursday and will run throughout the balance of the conference day. On Tuesday afternoon there will be no conflicting technical committee meetings or technical symposia so everyone will have an excellent opportunity to visit the exhibits and discuss with the exhibitors their new products and materials for use in the battle against corrosion. The exhibit will close Thursday night.

Entertainment

Harry Harner of Carpenter Steel Company, chairman of the Entertainment Committee, has made arrangements for the Fellowship Hour and Annual Banquet to be held in the Gold Room of the Fairmont Hotel. The Fairmont Hotel, high atop Nob Hill in San Francisco, is a show place and the Gold Room is one of the most beautiful banquet facilities on the West Coast. In addition to the usual fine menu and interesting after-dinner program which has been a tradition of annual banquets of the NACE, he promises top entertainment and a wonderful evening of dinner dancing following the banquet in one of the most beautiful "eveing out" atmospheres available anywhere in the United States.

In addition to the activities which Mr. Harner's committee has planned, the City of San Francisco offers top attractions in both entertainment and cuisine. Restaurants of all types serving specialty dishes from all over the world can be found in San Francisco and the variety and quality of facilities for dining out are unequalled. In addition, during the week of the annual conference in March, the theatre and concert program will be varied and attractive.

Transportation

Traveling to and from San Francisco from anywhere in the United States should not only be easy but pleasant. San Francisco is served by four principal transcontinental air lines and air travel on non-stop or one-stop schedules is available from the 60 largest cities in the United States. The selection of routing will permit lay-overs at other West Coast cities such as Los Angeles, Portland and Seattle at little or no extra cost. Alternate routes are available to enable the traveler to view such items of scenic interest as the Rockies, Grand Canyon, Donner Summit, Lake Tahoe and Yosemite Valley.

In addition to the excellent air travel facilities into San Francisco, the city is served by three principal transcontinental passenger railroads with connections to all important cities of the United

Busiest Technical—

(Continued From Page 126)

States. Here again, the selection of available routes permits the maximum in sightseeing opportunities with interesting scenery available overland from Omaha and Ogden through Donner Summit; from Kansas City, Denver and the Feather River Canyon; or from the South through Arizona, New Mexico and Southern California. In addition to this direct service into San Francisco, connections are available through Portland and Seattle across the northern portion of the United States through beautiful country in Montana and Northern Idaho.

Aside from the opportunities offered by transcontinental travel to and from San Francisco, Bob Culver of Coulter Steel and Forge, chairman of the Transportation Committee, has made arrangements through Matson Navigation Company and United Air Lines for a postconference tour of Hawaii for members who wish to extend their conference travel to include an island vacation. More details on this program will be released directly from Matson and United to the membership of the association, but the advance information indicates that the Hawaiian vacation planned for us by these firms will be an event long to be remembered.

Housing

For some four years, the conference committee has had hotel space in the top San Francisco hotels under contract for the conference. Chairman Les Habben of Ryerson Steel has worked with the San Francisco Housing Bureau to prepare housing applications which are now at the printer. It is anticipated that these applications will be mailed out to the membership of the association early in December. The Housing Bureau, working with Mr. Habben's Committee, has arrived at a smooth method of operation which will enable each member to obtain housing in accordance with his desires as promptly as possible and with a minimum of confusion. There is an adequate supply of housing in San Francisco and no member need be concerned about availability of hotel space

Registration

Chairman Phil Raifsnider of Shell Development indicates that advance registration cards will be mailed out with the housing applications in early December.

Registration will be conducted in the Fairmont Hotel on Sunday afternoon and all day Monday and will move to the Civic Auditorium Tuesday morning. Registration will be open all through the week at the auditorium from Tuesday morning through Thursday evening.

Ladies Activities

The natural appeal of San Francisco as the commercial center of the West will be supplemented by Chairman Jack Pappas of Electric Steel Foundry Company and his committee who are busy planning special events for our lady guests. Jack's list of available opportunities for the ladies includes excursions to local points of interest and a peak into some of the romance of the trade to the Orient. Members are urged to make every effort to have their wives accompany them to San Francisco because not only the special program for ladies planned by the committee, but also the natural attractions of San Francisco will make attendance a memorable event.

TITANIUM—available <u>now</u> for long service
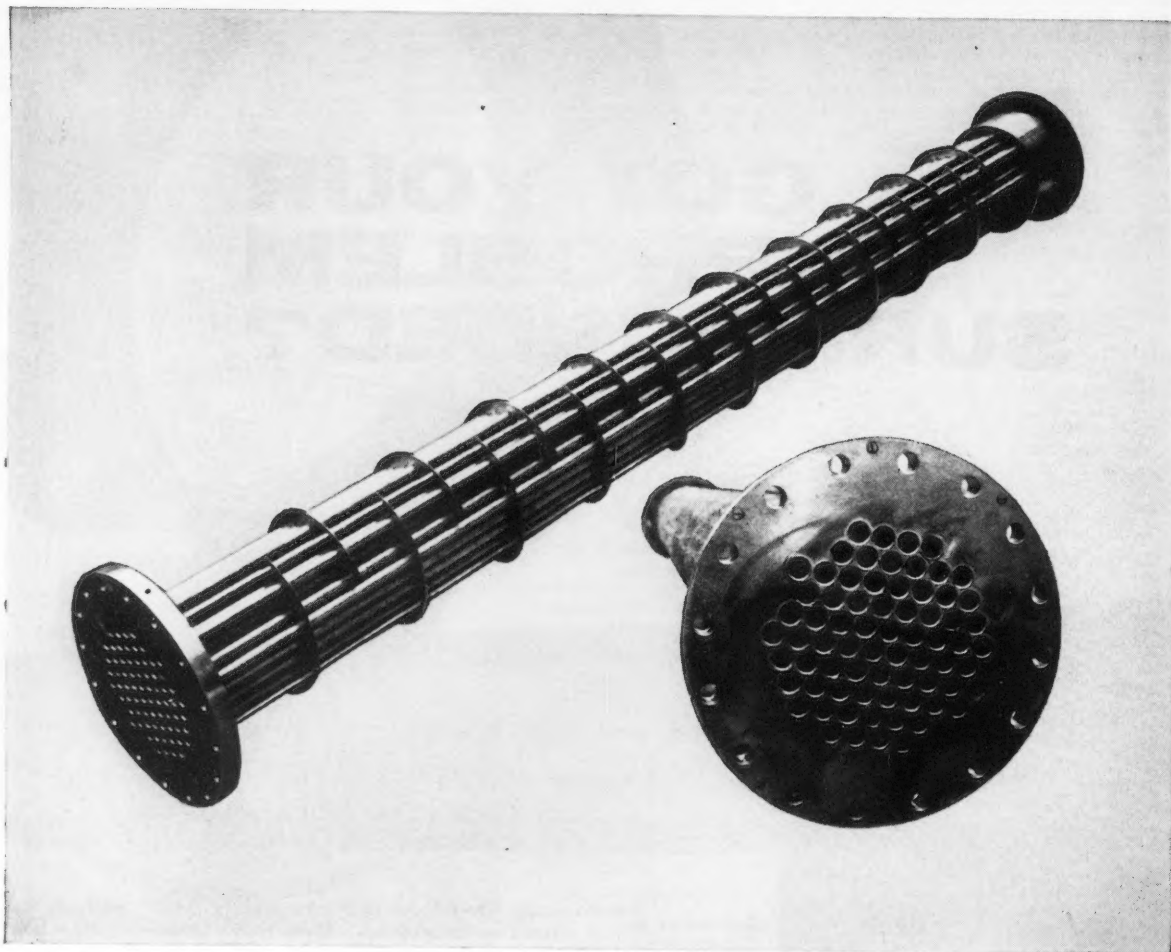
• *The life of this titanium 70-tube condenser assembly, now handling 60% nitric acid at 195° C. and 180 psi, is estimated to exceed 10 years.*

Titanium condenser tubes expected to outlast stainless 30 to 1 handling nitric acid

Corrosive vapors of 60% nitric acid gnawed through an average of three stainless-steel tube bundles a year in a chemical firm's condenser. Maintenance and replacement costs were running as high as $18,000 a year. Then titanium tubes were installed. Based on a service life of 10 years, titanium will save at least $162,000 in maintenance and replacement costs.

San Diego Section—

over half of those returning inquiry cards indicated they would attend, according to Kenneth R. Christy, Federal Housing Administration, registration chairman.

The four-session night school on basic corrosion was attended by 31 students with a faculty staff of 8. Students came from many fields and expressed appreciation for the courses. Classes started Sept. 12 at the Alvarado Filtration Plant, City of San Diego Water Dept.

There were two technical speakers at the September meeting at Lawton's restaurant in La Mesa, Cal. James Burton, director, West Coast Laboratory, Culligan, Inc., San Bernardino, Cal., reviewed corrosion problems in water softening equipment manufactured and leased by the Culligan Co. He outlined various measures used in the past and now being used to prevent or minimize corrosion. Otto Waters, San Diego Water Department, presented a paper on "Alternating Current Corrosion." His paper discussed pros and cons of grounding electric services to water mains. He described tests and research concerning this controversial subject. A paper further discussing the subject was scheduled for the Western Region meeting.

F. N. Alquist

Francis N. Alquist, a member of the National Association of Corrosion Engineers since 1947 and for 28 years employed by The Dow Chemical Co., Midland Mich. died while at work September 25. Dr. Alquist, an authority on corrosion problems in the chemical, petrochemical and allied industries, was a member of the Edgar C. Britton Research Laboratory staff.

Long active in NACE, at the time of his death he was chairman of Technical Committee T-3C on Annual Losses Due to Corrosion. He had been chairman of the NACE editorial review subcommittee and for many years was a member of the committee. His other activities in the association included work on technical programs at various meetings over the country. He consistently attended national NACE conferences and was author of many papers on corrosion control published in CORROSION and elsewhere as well as holder of 24 patents.

New Telephone Number

CENTRAL OFFICE NACE

is

CApitol 4-6108

Have You Noted The Technical Topics Section?

In every issue of CORROSION a "Technical Topics" section is published. It includes timely technical information likely to interest you. Turn to Page 141 this issue.

GENERAL NEWS

29 British Schools Have Corrosion Courses

Subjects Covered Show Interest Is Over Wide Field

Courses, classes and short courses on corrosion control are reported by 29 British universities, colleges and technical schools in a report compiled by I. W. Stubbs, honorary secretary of the Education Panel of the Society of Chemical Industry. The report, supplied to the National Association of Corrosion Engineers through F. L. LaQue, The International Nickel Co., Inc., New York, who presented a paper before the society in 1955 on corrosion courses in the United States, is a follows:

Summary of Courses on Corrosion Available in the United Kingdom

Barnsley, Mining and Technical College—Corrosion in its physico-chemical aspects is dealt with in courses for the Higher National Certificate in chemistry and for the ARIC.

Birmingham, The University—Corrosion figures prominently in metallurgy courses. Second year physics and chemistry of metals and second year general metallurgy each have a course of 24 lectures, approximately one-sixth of the total time being concerned with corrosion. In the third year, metallurgical technology, ten of the total 38 lectures are devoted to corrosion and the theories underlining corrosion protection. In the Department of Chemical Engineering corrosion is dealt with in some detail in the fourth year course. In addition, short courses of lectures by visiting corrosion authorities are arranged as opportunity offers. **College of Technology**—A short course on Fundamentals of Corrosion Science, consisting of seven lectures by visiting lecturers, was given in the early part of 1956.

Bradford, Technical College—Course entitled "Corrosion and Surface Treatment" available to day release and evening students. A residential course under the auspices of the Yorkshire Council for Further Education, Metallurgy Advisory Committee, is expected to be held in October, 1956.

Burnley, The Municipal College—Corrosion forms part of a course in electroplating and a course in metallurgy for Higher National Certificate. In 1955 a course of six lectures on corrosion was given by Dr. Axon of the University of Manchester.

Cambridge, The University, Department of Metallurgy—Natural Sciences Tripos Part I, Metallurgy—four out of 64 lectures for metallurgy half-subject are on corrosion. Natural Sciences Tripos Part II, Metallurgy—16 lectures on corrosion and protection of metals in a total of 160. Seven lectures dealing with electrodeposition and another three with the preparation and properties of other types of metallic coating are included in a course entitled "Chemical Metallurgy." Regular corrosion lectures

have been given since 1938. Research facilities are available.

Chesterfield, College of Technology—Corrosion and protection of metals are dealt with in metallurgy courses for the Higher National Certificate in Metallurgy and Mechanical Engineering and in Advanced Physical Metallurgy for the Institution of Metallurgists.

Dundee, Queens College—Corrosion will be included in a possible new combined course in chemistry and engineering.

Edinburgh, The University—Ten lectures on corrosion are included in the final year course in technical chemistry. With the new degree of chemical technology it is probable that the sub-course on corrosion will be extended. **Heriot-Watt College**—A few lectures and simple demonstrations on corrosion are given in the Metallurgy and Dentistry classes.

Glasgow, Royal Technical College—Lectures on corrosion are part of the Technical Chemistry Course. In the winter of 1956-57 a course on corrosion in the late afternoon will be offered and, if successful, can be extended in subsequent years.

Huddersfield, Technical College—In 1955 an advanced lecture course of eight lectures on corrosion was held in association with Yorkshire Council for Further Education, and based on a similar course held at the Sheffield College of Technology.

Ipswich, School of Technology—Corrosion forms part of courses in chemistry and metallurgy for Higher National Certificate and ARIC.

Leeds, College of Technology—It is possible that a special course in corrosion may be offered next year.

Liverpool, The University—A special course of lectures on corrosion and oxidation is given in the Department of Metallurgy by Dr. S. J. Kennett. A synopsis of the course has been provided. Two lectures on corrosion are also included in an introductory course for engineers and second year metallurgists.

Llanelly, Technical College—Would be pleased to accommodate lectures on corrosion.

London

Acton Technical College (Middx. C. C.)—Corrosion forms part of the syllabus in courses for marine engineering and metallurgy for ARIC and Higher National Certificate for Mechanical Engineering. Corrosion is to be a main subject in the proposed new Sandwich Course in Metallurgy.

Battersea Polytechnic—Day and evening courses in corrosion/surface treatment are available in the Metallurgy Department for the AIM and Higher National Certificate. A post-graduate evening course is proposed for 1956-57 and a summer school on water treatment will be held in 1956. Research facilities are available.

Borough Polytechnic—Specialise in courses on paint technology in which prevention of corrosion and decay are

given special attention. Would be willing to receive suggestions for courses from the panel.

Imperial College of Science and Technology—Three one-hour lectures on corrosion are given to third year metallurgy students at which occasionally part-time students could attend.

Northampton Polytechnic—A special two year co-ordinated course in corrosion is given for those wishing to obtain a broad treatment of the subject. Corrosion is also included in the metallurgy course for the examination of the Institution of Metallurgists and a metal finishing course for the City and Guilds examination. Corrosion is dealt with in all chemistry classes given to engineers and in part-time courses on fuel technology. Both part-time day and evening classes are available.

Norwood Technical College (LCC)—No courses on corrosion but consider that a special course in "Microchemical Techniques" might be of value to a metallurgist working in the field of corrosion.

Queen Elizabeth College—Corrosion is included by the Household Science Department in courses on cookery, laundry work and household management, and also by the chemistry department in lectures on water in the household and detergents.

Regent Street Polytechnic—Corrosion forms part of a course for chemistry and engineering diploma students and will also be studied by chemistry diploma students in a new scheme of which details are not yet available.

University College—Courses on materials of construction and physical chemistry are specially arranged to deal with basic electrochemical principles, generally in accordance with the syllabus published by the Institution of Chemical Engineers.

Manchester, College of Technology—Corrosion is dealt with in considerable detail in both the chemical engineering and metallurgy courses and also forms part of all chemistry courses.

Monmouthshire, Technical College, Crumlin—Corrosion is included so far as courses for examinations for Ordinary National Certificate in Metallurgy and Higher National Certificate in Chemistry and the ARIC are concerned.

Nottingham, Technical College—Corrosion is part of the course preparing for the Institute of Metallurgy Examination.

Salford, Royal Technical College—Corrosion forms part of engineering and metallurgy courses for the higher National Certificate and Higher National Diploma.

Southampton, The University—The course on chemistry for first year engineers includes six lectures on corrosion.

Swansea, University College—Corrosion forms part of the electrochemical course for pass degree and honours degree students in chemistry and the course in electrometallurgy for honours students in metallurgy.

Equipment Services   NEW PRODUCTS   Materials Literature

Adhesives

Bonding polyethylene to brass, natural rubber and some synthetic elastomers is now possible with an adhesive developed by Bell Telephone Laboratories, 463 West St., New York 14, N.Y. Bonding, accomplished with heat ranging from 250 to 350 F. and pressures of 100 psi or less may be extended to plastics related to polyethylene the laboratories believe. Use of the adhesive to bond polyethylene directly to metals will be helpful in protecting them from corrosives.

•

Metalset A4, a product of Smooth-On Manufacturing Co., 572 Communipaw Ave., Jersey City, N.J., an aluminum filled epoxy resin compound comes packed in two collapsible tubes. Proper quantities are measured by squeezing out identical lengths of material from tubes and mixing them. It is suitable as a caulking compound and will adhere to wood, metals, plastics and concrete and is suitable for use as an adhesive between these materials and between glass.

Aluminum

Foil and Packaging Division, Alcoa Research Laboratories, New Kensington, Pa. will do fundamental research on foil packaging problems.

Atomic Energy

The Institute of Nuclear Energy's research reactor, built by Babcock & Wilcox Co. on the campus of University of Sao Paulo, Brazil, is the first reactor activated in South America.

•

Alco Products, Inc., Schenectady 5, N. Y. will build three intermediate sodium heat exchangers for the $54 million Enrico Fermi nuclear electric generating station near Detroit. Each will be about 6-foot diameter by 30 feet and will weigh 124,000 lb.

Cathodic Protection

Corrosion Rectifying Co., Houston has started installation of rectifier corrosion protection systems on 157 oil well casings for the Pan American Petroleum Corp. in the Elk Basin Field of Wyoming.

Cleaners

W and W Instant Grease and Oil Remover Concentrate, marketed by Wilbur & Williams Co., 130 Lincoln St., Brighton 35, Mass. leaves no unpaintable film, is odorless, non-toxic, inexpensive and mixes with hot or cold, fresh or salt water, according to the manufacturer.

Coatings

Porcelox, a water-base, semi-organic, semi-porcelain ceramic resistant to corrosives up to 1100 F is suitable for use in coating exhaust manifolds, pipes, mufflers and metals subjected to high temperatures. Curing is at 450 F for 15 minutes or longer, dependent on mass. It is made by Kraus Res. Labs, Cockeysville, Md.

•

Spee-Flo Company, 720 Polk St., Houston has named Paul E. Moss and Co., 152 West 65th St., New York 23, N. Y. as its export representatives.

•

Koropon finishes manufactured by De-Soto Paint & Varnish Co., Garland, Texas are described in a 4-page illustrated brochure.

Education

The International Nickel Co. has established a chair in Chemical Metallurgy at Columbia University with an endowment of $350,000.

•

Temco Aircraft Corp. supplies experienced aircraft engineers to teach one hour of physics daily to high school classes at four Dallas area schools. About 100 students are benefited.

Fuel

Metal Hydrides sodium borohydrite plant of Badger Mfg. Co., Danvers, Mass. will make high energy fuels under Navy contract. Hydrogen, sodium and methanol are the raw materials.

•

Hydrogen and Oxygen are used as fuel in a new fuel element developed by Research Laboratories of National Carbon Co., Union Carbide Corp. The element is providing silent electrical power for the U. S. Army Signal Corps "Silent Sentry" radar.

Fittings

Speedline formed fittings for lightwall stainless pipe are designed to make tight joints in an economical, leak-proof system according to H. T. Potts Co., 504 Erie Ave., Philadelphia 34, Pa.

Instruments

Beckman all-transistor analog-to-digital converter is described in a bulletin available from Beckman Instruments, Inc., Systems Division, 325 North Muller Ave., Anaheim, Cal.

•

Remote Control welding of highly radioactive materials into stainless steel capsules is possible in a new unit developed at the Oak Ridge National Laboratory, Oak Ridge, Tenn. It uses an inert gas shielded arc welding torch.

•

Mark 1-F4 linear electron accelerators emitting high energy electrons, X-rays or neutrons as desired are available in electron beam strengths from 2 to 10 million electron volts. A descriptive brochure on the Arco Linear Accelerator is available on request from Applied Radiation Corp., Walnut Creek, Cal.

•

d/M-Gauge, a portable instrument that gives two minute readings of the moisture content of materials is available from Nuclear Chicago Corp., 229 West Erie St., Chicago 10, Ill.

•

Atkomatic Valve, Inc., 545 W. Abbott St., Indianapolis 25, Ind. is making a two-way Type 316 stainless steel solenoid valve rated to 6000 psi.

•

Aquavox, a high frequency compressional wave system designed for underwater communication between divers in aqualungs has been developed by Cotton Associates, Inc., 4312 Main St., Philadelphia. The almost weightless device permits communication at ranges up to ¾ mile at depths to 200 feet. It fits into any full mask type Scuba.

•

Instrument Division, Robertshaw-Fulton Controls Co. has developed a Land Radiation Pyrometer which measures radiant energy given off by hot objects permitting temperature measurements without physical contact with the object.

•

Narda Microwave Corp., 160 Herricks Rd., Mineola, L. I., N. Y. has formed a subsidiary to make ultrasonic cleaning devices.

Metals—Ferrous

Electro Metallurgical Company, a Division of Union Carbide Corp. has established a Fine Metals and Chemicals Division at Niagara Falls, N.Y. The new division will be responsible for the manufacture and sales of new alloys, pure metals, metal chemicals and other products.

•

Data Sheets on new corrosion resistant casting alloys are available from Alloy Casting Institute, 286 Old Country Road, Mineola, N.Y. at $1 a set.

•

Stainless, alloy and carbon steel universal plate is now available in 12 to 36-inch widths from A. M. Byers Co.

•

Stainless Steel hydroelectric turbine blades weighing 35,000 pounds were cast by S. Morgan Smith Co., for two Kaplan hydroelectric turbines units to be installed on Brazil's Rio Grande River next year. Reduction of corrosion and cavitation pitting is expected.

Metals—Non-Ferrous

Ampco Metal, Inc. will build a $200,000 branch foundry at Garland, Texas. It will become principal sales and service office for the company in the Southwest.

•

Lithium Alloys of aluminum developed by Alcoa Research Laboratories will maintain high strength up to 400 F.

•

Tantalum-Columbium facilities of Fansteel Metallurgical Corp. near Muskogee,

NEW PRODUCTS

(Continued From Page 134)

Okla. which go into production this year will materially increase the supplies of these metals.

Mallory Sharon Metals Corp., a $55 million corporation owned by Sharon Steel, National Distillers and Chemical Corp. and P. R. Mallory & Co., Inc. will engage in the manufacture and marketing of titanium, zirconium and other light metals.

Non-Metallics

Karbate impervious graphite shell and tube heat exchangers are being made in three new sizes, 8, 42 and 45-inch diameter shells by National Carbon Company, Division of Union Carbide Corp. They are described in catalog section S-6800.

Asbestolux, a long fiber asbestos bonded chemically with special silica, is a lightweight and incombustible building board available from North American Asbestos Corp., 141 West Jackson St., Chicago 3, Ill.

Plastics

National Petro-Chemicals Corp. will build its second polyethylene plant on a 200-acre site on the Houston Ship Channel. It will produce about 75 million pounds annually of intermediate density polyethylene. The materials will be marketed under the name Petrothene by U. S. Industrial Chemicals Inc.

Byers PVC, polyvinyl chloride plastic pipe will be marketed nationally by A. M. Byers Co. in sizes from $\frac{1}{4}$ to 6 inches. Both types will be available in three wall thicknesses.

Teflon is used to make molded porous filter cups up to 12 inches high with a 5-inch inside diameter by Porous Plastic Filter Co., Inc., a Pall Filtration Company, Glen Cove, N. Y.

Fluorulon Laboratories, Inc., P. O. Box 305, Caldwell, N. J. is making Fluoroma laminates of Kel-F reinforced with glass fiber grids and Fluoroglas which use 15-18 percent by weight of pulverized glass filaments

Southeastern Plastics Sales Co. of Atlanta, Ga. has been named distributor for Resistoflex Corp. in several Southeastern states.

Teflon 100-X perfluorocarbon resin film will be manufactured by duPont in sample quantities to supplement other packaging films made by the company. The film is capable of continuous service at 400 F, is heat sealable and inert to most chemicals. Extensive use for tank linings is forecast.

A New Saran lining for use in handling chemicals has been developed by Saran Lined Pipe Co., Ferndale, Mich. Pumps, valves, pipe and fittings are now available lined with the new material at no advance in price over the older Saran.

VYHH Type vinyl resins will be produced by Bakelite Company at a 30 percent increase in quantity when new Texas City facilities are completed.

CASING IN 62 OIL WELLS PROTECTED FROM CORROSION

Here's how an oil producing company on the Gulf Coast stopped external casing corrosion on 62 of its wells. Five of the wells were in a salt water bay.

Potential-drop profiles indicated that cathodic protection could be applied to the total depth of 5,500 feet. CSI determined the current requirements, using the log current-potential method.

Then CSI engineers designed and installed a protective system for each well based on a guaranteed current output. The range of current requirements was from 0.5 to 6.2 amperes. The necessary current was delivered from ground beds each containing from two to 16 magnesium anodes. Galvomags, Dow's new high potential anodes, were used in special lengths to provide 10-year installation life at the lowest possible cost. This cost ranged from $215 to $510 per well.

Call or write today for estimates or quotations on your cathodic protection needs—materials or services. No obligation.

CSI

CORROSION SERVICES INCORPORATED
Tulsa, Oklahoma

P. O. Box 7343, Dept. A-11   Telephone: Circle 5-1351

MEN in the NEWS

Joseph S. McCulloch has been named Northeast district manager for Tube Turns Plastics, Inc. with headquarters at Riderwood, N. J.

Roger J. Amorosi, president of Parameters, Inc., New Hyde Park, N. Y. is chairman of the Second Annual Technical Meeting of the Institute of Environmental Engineers, April 17-18 at the New Yorker Hotel.

Henry F. Sander, Chief Test Engineer, Vapor Heating Corp. has been elected president of the institute.

E. Q. Camp has been promoted to assistant division head, Research and Development Division, Humble Oil & Refining Co., Baytown, Texas. His duties include responsibility for the corrosion section. Besides NACE he is a member of the Air Pollution Control Association and API.

David W. Peake has become a partner in the S. D. Day Company, 3115 Buffalo Drive, Houston.

A. E. Pecore, has been named president of Humble Pipe Line Co., succeeding O. Q. Lomax. He is succeeded as vice-

MEN in the NEWS

(Continued From Page 136)

president by **William S. Spangler**, formerly general superintendent, while **P. D. Phillips, Jr.** has been made general superintendent and a director of the company.

•

Peter G. Dennison, president of Metal Spraying Corp., 3610 West Pierce St., Milwaukee 15, Wis, has been reelected president of the American Metallizing Contractors Association for a third consecutive term.

•

R. D. Bradford, vice-president and director of American Smelting and Refining Co. has been placed in charge of the company's Federated Metals Division.

Robert E. Burns has been promoted to senior mechanical engineering in the engineering division at Humble Oil & Refining Company's Baytown refinery.

•

Kelvin Sproule, formerly on the staff of International Nickel Co. of Canada, Ltd., Copper Cliff, Ont. has joined the Development and Research Division at Inco's New York office where he is concerned with effect of radiation in research.

•

Raymond T. Whitzel has retired as vice-president and general production manager of Aluminum Company of America following more than 42 years' service.

•

Kenneth O'Connor has been made sales manager for Tubular Lining Corporation's Southern Texas region.

Russell H. Coe is now Pittsburgh district manager of The Master Mechanics Company, Cleveland, producers of chemical preservatives and sanitary coatings.

•

Lawrence W. Cunningham has been promoted to the position of Southern region sales manager by Kelite Corporation. He lives in Beaumont, Texas.

•

Harry A. Riley, Jr. has been made sales manager of the wholesale division of Southwestern Plastic Pipe Co., Mineral Wells, Texas.

•

Donald L. Colwell has been elected vice-president in charge of laboratories and research for Apex Smelting Company.

•

Ralph D. Webb, head of the instrument department of Union Carbide Chemicals

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CORROSION ENGINEERING DIRECTORY

MEN in the NEWS

(Continued From Page 138)

Company's South Charleston, W. Va. plant has been elected to honorary membership in the Instrument Society of America

Samuel E. Tyson has been appointed stainless steels metallurgist by Carpenter Steel Co., Reading, Pa.

Arvil B. McKee is now assistant chief of the newly established Foil and Packaging Division of Alcoa Research Laboratories, under Dr. M. A. Miller, chief. Mr. McKee currently is chairman of Pittsburgh Section NACE.

William J. Snyder has been named special sales representative of Tube Reducing Corp. to handle the company's nickel-alloy coating process marketed under the trade name "Niphos."

S. B. Hodges, marketing manager for Dresser Industries will coordinate activities of the firm's Plastic Products Department, recently established to develop and market plastic products for joining, repairing and maintenance of pipe. **H. Z. Hight,** Regular Products Sales Manager for Dresser since 1945 has been named president of Bonded Products, Inc., Orange, N. J. whose Epi-Seal products are marketed by Dresser.

Luther L. Yeager, a vice-president of Bjorksten Research Laboratories for Industry, Inc. is in charge of the company's Texas laboratories located at 2405 Norfolk St., Houston.

Albert H. Cooper has been named general manager of American Industrial Chemical Co., a Division of Amerace Corp., 93 Worth St., New York 13, N. Y. producing silica jells and other silicas.

I. W. Wilson has been named chairman of the board and **Frank L. Magee** president of Aluminum Company of America.

Robert B. Scrimgeour has been appointed manager of the Chemical Sales Department of The Pfaudler Co, Rochester, N. Y. **James P. Voorhies** has been named sales engineer in the company's Houston sales office.

P. R. Donnelly is a new sales representative for Plastic Applicators in the Houston area.

Joseph A. Neubauer has been elected president of Columbia-Southern Chemical Corp. A chemical engineer, he graduated from Case Institute of Technology in 1932.

Arthur W. Huff, Jr., a physicist, has joined the Metal Physics Section of the Metallurgy Division at the National Bureau of Standards.

Frederick W. Fink has been named chief of the Corrosion Research Division at Battelle Memorial Institute, Columbus, Ohio. He joined the institute in 1938.

L. I. Dana has been appointed vice-president—research and development and **David Swan,** director of research of Linde Co., a division of Union Carbide Corp.

H. Clay Howell has joined the staff of Miller-Warden Associates, asphalt consultants, Swarthmore, Pa. He formerly was on the technical staff of Pioneer Asphalt Div., Witco Chemical Co. and for many years was with the Barber Oil Corp. as chief chemist.

John D. Kleis has been appointed vice-president and director of research of Fansteel Metallurgical Corp., North Chicago, Ill.

Richard B. Kropf has been named supervisor of development activities in the automotive industry, Development and Research Div., The International Nickel Co., Inc., New York. He will continue to make his headquarters at the company's Detroit field office.

Aubrey M. Callis has been appointed general sales manager of American Smelting and Refining Co., Federated Metals Div. **J. L. Kammermeyer** will become general sales manager of the new Central Aluminum Dept., leaving his post as manager of the Houston plant. **R. A. Colton** will replace Mr. Kammermeyer at Houston.

A. Gregg Noble is new assistant to the director of operations, Solvay Process Division, Allied Chemical and Dye Corp. He has been manager of Solvay's Mutual Chemical Div. plant at Baltimore.

John F. Beck has been named metallurgist supervisor of technical service; **Clark P. Church** metallurgist supervisor of process development and **John F. Ewing** metallurgist supervisor of research of Babcock & Wilcox's Tubular Products Div.

TECHNICAL TOPICS

Chemical Surface Preparation of Structural Steel After Erection*

A SYSTEM has been developed in Britain as a complete pretreatment consisting of carrying acid pickling to the site: A range of descaling jellies, each designed for a broad category of work, which have as their bases the three main acids used for bath descaling—hydrochloric, sulfuric and phosphoric. These jellies adhere to vertical surfaces for sufficient time to loosen all the scale layers, which are then removed by scraping, wire brushing or power hosing.

An advantage is that the scale may be left on the steel until after erection, so that the danger of severe rusting of the steel beneath the scale layers is reduced.

Another advantage is it is simply applied by brush or spray equipment and left to react. Processing times vary between 4 and 24 hours according to the nature and condition of the scale. This treatment etches the steel surface but does not bite into the substrate or open up the grain structure of the steel as does flame descaling.

If phosphoric acid-based jellies are used, the steelwork will require no neutralizing, surfaces may be wire-brushed and the sludge, comprising exhausted jellies and dissolved scale, wiped away with cotton waste. In the case of hydrochloric or sulfuric acid-based jellies, this procedure is augmented by hosing down.

Rust Film Is Formed

Steelwork always is allowed to weather for about 24 hours, sufficient time to develop a light film of rust, which is a desirable preliminary to the rust inhibitory treatment which follows.

The process which follows descaling is based on phosphoric acid, with which are blended inhibitors, accelerators, surface activators and other agents. It differs from two percent phosphoric acid treatment in a number of ways. It is self-neutralizing, requires no water rinsing, removes rust and, by reacting with basis metal, deposits a water insoluble, impermeable, amorphous phosphate coating on the steel.

After derusting, the steelwork is drained to remove surplus solution and dried. The process is applied cold to structural steelwork by brush or spray.

Coating Matures Slowly

A further property is vital to successful preparation of structural steelwork for painting. In contrast with conventional phosphate processes, the coating

Abstract

A method of removing millscale and preparing for coating structural steel by the application of chemicals after erection is described. Production of a phosphate coating by application of chemicals to chemically cleaned steel after erection is possible with materials developed in England and used extensively there. Some economic data indicate the cost of surface preparation by the chemical method has some advantages over sandblasting.

does not attain full maturity until about 30 days after processing although the primer coat is applied little more than an hour after derusting. The coating achieves full development incorporated with the primer; and forms on the surface of the steel and in the grain structure.

The derusting operation, as with painting, must be done in dry weather, because the balance of the processing solution may be adversely affected by rain.

Derusting and phosphating takes little more time than application of lead paint. The problem is in excluding moisture from the phosphate coating during drying and hardening, when rain or early morning dew could harm it. To overcome this, special sealing media have been developed for application by brush or spray while the processed surfaces are still damp and the phosphate coating is beginning to form. They reduce the time between phosphating and painting and the possibility of contamination of treated surfaces. The sealing media combine with residual solutions to form strongly rust-inhibitive foundations for painting. Sealers of this type are not intended to replace primers.

Pretreatment of steelwork as described will take longer than other methods.

Application Speed Is Critical

Processing time refers to the descaling of 1 sq. ft. or 301 sq. ft; the significant factor on a big structure being speed of application rather than speed of chemical reaction. Thus, where a large quantity of steel is involved, chemical descaling may be considerably more rapid than mechanical descaling.

Chemical treatments are so far superior to other means as to outweigh their drawbacks. This system is used widely in England under government specifications on such work as atomic power stations, British Electricity Authority plants, wind tunnels and other airport structures and a variety of similar Ministry of Works projects, in addition to ships, bridges, gasholders, factory building and similar industrial undertakings. Derusting and phosphating and the sealing media are used for treatment of new steel and for renovation of corroded structures.

Based on the assumption that one U. S. ton of steel (2000 lb.) represents 250 sq. ft. of surface, it is estimated that sandblasting to NACE No. 2

standard would cost a minimum of $30 a ton. Complete chemical treatment (descaling, derusting, phosphating, and sealing) and cost of washing down and a due proportion of scaffolding costs, averages $38 a ton, including both material and labor charges. The breakdown of this figure is: $25.20 for descaling and washing down; $5.70 for derusting and phosphating; and $7.10 for sealing per ton. It will be noted that jelly descaling is by itself considerably cheaper than sandblasting.

The chemical treatment described is designed to work in conjunction not only with protective coatings but with the various forms of cathodic protection. The system described removes mill scale and rust. It also deposits a nonconductive amorphous phosphate coating which imparts a high degree of electrical resistance to the surface.

The amorphous coating achieves 100 percent coverage of the steel surface, in contrast with most equivalent crystalline coatings and virtually eleminates sites susceptible to electrochemical attack.

DISCUSSIONS

Question from J. H. Carroll, Olin Mathieson Corp., Niagara Falls, N. Y.:

What is the composition of the vehicle jelly used for steel surface conditioning?

Reply by Henry W. Adams:

I have not been informed by Jenolite as to the vehicle composition. However, it is apparently an emulsion type which is designed to hold the active agents: Phosphoric acid: DJ/1; sulfuric acid: DJ/2; or hydrochloric acid: DJ/3, on the surface and without drying out long enough for them to attack and loosen the mill scale. These vehicles have no other function.

Question from James W. Sheffer, Philadelphia Quartz Company, Philadelphia:

Is the phosphate layer thus formed susceptible to leaching out when immersed in water, or exposed to steamy atmospheres?

Reply by Henry W. Adams:

I believe this refers to the rust removing and neutralizing treatment applied **after** the steel has been de-scaled and weathered. The amorphous iron phosphate coating which is thus formed is impervious to moisture and is insoluble in water after it has completely matured. However, since this process requires up to 30 days and continues after the paint system has been applied, it will be seen that it is quite vulnerable to moisture for the first 30 days. Therefore, for practical purposes, the answer is "Yes."

Question from H. A. Pace, Duquesne Light Co., Pittsburgh:

Are jellies recommended for the removal of heavy corrosion products?

Chemical Surface—

Reply by Henry W. Adams:

The products referred to are presumably acid salts and other deposits; heavy oxides in scale formation and possibly chlorides which have penetrated the grain structure of the metal. The jelly application will accomplish several things: a) will dissolve and remove heavy oxides; b) by reason of the washing down operation will remove soluble deposits such as salts from the surface. The jellies themselves would have no more effect than does sand blasting upon chloride penetration.

The washing down process would, however, at least partially remove the chlorides in the substrate and the neutralizing and passivating process which follows would complete the decontamination. We shall be glad to submit considerable data on this phase, if requested.

Question from Austin Long, The Glidden Company, Reading, Pa.:

How does the application of phosphating treatment affect adhesion of paint systems over old paint which may have been covered by a layer during phosphating of bare and rusted adjacent areas?

Reply by Henry W. Adams:

The phosphating process described actually forms an amorphous coating over all surfaces to which it has been applied and is tenaciously adherent. Moreover, the specifications call for wiping off all surplus material before it dries. In our experience, any material remaining on top of patches of old paint which are left on the surface does not interfere with adhesion of subsequently applied paint systems, provided the phosphated surface has been allowed to dry. This usually takes one hour, unless drying is prolonged by unfavorable conditions of temperature and humidity, when more time will be required.

Question from Seymour J. Fiebach, Carboline Co., New York:

How does this system compare with well-known phosphating processes like Bonderizing, Granodizing, etc.?

Reply by Henry W. Adams:

The end result—removal of rust and passivation of the steel—is the same. The difference is that the processes mentioned are for hot application by immersion. Admittedly, these processes, and Jenolite, too, are far more efficient when applied hot. The Jenolite process, originally developed for hot application, has been modified and adapted for cold application to steel-work in situ. Thus, there can be no real comparison since these products are formulated for use under entirely different conditions of application.

TECHNICAL TOPICS for DECEMBER

Urethane Coatings, Structure, Characteristics and Uses by Richard C. Burck.

Some Keys to Successful Industrial Contract Painting by L. L. Sline.

Spray Injection of Liquids into High Pressure Gas Line by F. E. Blount and J. W. Anthony.

Epoxy Coatings Perform Well on Steel Exposed to Chemicals, Corrosive Atmospheres*

Abstract

Case histories are given of successful use of epoxy coating systems on steel surfaces exposed to chemicals and corrosive atmospheres. Equipment coated includes floating roof type tanks, solvent tanks, paper mill tanks and structural steel. Good performance in competition with other generic types is reported for periods up to 5 years is reported.

EXAMINATION of epoxy-type coatings shows good results were obtained in installations involving problems common to many industries. Some installations are in areas where other paint coatings are used commonly and others where no paint coating had, before the epoxies, performed properly. These applications vary in age and establish epoxies as very useful tools to prevent corrosion.

First installation considered involves floating roof-type gasoline tanks. Three and one-half years ago a leading oil company found excessive corrosion on its floating roof storage tanks. The damage was so severe that tanks which normally had a life expectancy of 15 to 20 years were being replaced in as short a time as five years. The cause of the corrosion was believed to be the weather, gasoline additives, alternating wet and dry cycles and removal of protective rust by the roof shoes. An amine-cured epoxy coating was used and showed considerable promise in prolonging life of the tanks a few years. Cost of the application, based on a projected life of three years, was economical.

A second installation was selected because it was a competitive test of general maintenance coatings. Epoxies were applied over wire brushed surfaces and results exemplified their weathering properties.

Solvent Tanks Test Coatings

A company in the Midwest had ten solvent tanks that required continual paint maintenance, so it called on several paint companies asking that the best paints available be submitted for testing. Each of the appointed suppliers was given two tanks to paint. Contents of the tanks were highly flammable so they could not be taken out of service. Surfaces were wire brushed.

An amine-cured epoxy primer and two finish coats of amine-cured epoxy were applied to one tank. On another tank, a coat of modified epoxy ester primer and two coats of the modified epoxy ester finish coat were applied.

Eight other tanks were coated with top quality alkyd and oleoresinous materials from four other paint manufacturers.

At the end of the year, one of the oleoresinous coatings had failed. At the end of three years, all eight tanks coated with other than epoxy coatings had failed.

At the end of five years an inspection was made of the two epoxy tanks to determine which of the two systems would be used to repaint the other eight tanks. Both the ester and the amine-cured epoxies were in excellent condition. Although the amine-cured epoxy finish showed more chalking than the ester, there was very little film erosion.

The chalking, although rapid between the first and the second year, had become dormant. The epoxy ester was used to repaint the eight tanks.

These installations are now six years old and admittedly would have been in better condition had the tanks been sandblasted. They have, however, shown a 2 to 1 life improvement over other generic type coatings in spite of imperfect surface preparation.

Continuous Water Immersion Test

The third installation was selected because it was in continuous water immersion.

A paper company wanted a satisfactory coating for the inside of a metal water purification plant, called an accelator. When data on the epoxies was asked, the company was shown laboratory tests and told of small field-test results indicating formulations of amine-cured epoxy finishes were satisfactory for water resistance. Although no large installation involving water resistance had been coated, the epoxy showed more promise than systems previously tried unsuccessfully.

Airless hot spray equipment was selected for application and formulations were found satisfactory for this method of application.

The accelator was sandblasted and primed with an amine-cured epoxy primer. Representatives of manufacturers of equipment and paint were on the job to instruct the painters in proper methods. Pot-life of the material was over five hours at 180 F and 600 psi liquid pressure. Three coats of amine-cured finish coat were applied to a thickness of 8 mils.

A suitable solvent was used with the hot spray equipment because thinners normally used for amine-cured epoxy coatings evaporate too fast and do not allow proper flow or proper adhesion between coats.

This application was made in very good drying weather with afternoon metal temperature approximately 130 F.

At the one-year inspection, a spot was found with no adhesion. Investigation showed the primer had been applied over a heavy sand dust left by the nearby sandblasting operation. This was repaired and shows no further damage after two years. No rust or water was found under the peeled film.

Resistance To Condensation

Another accelator exterior in Mississippi was sandblasted while out of service and coated with this same system. This tank is subject to condensation in the summer months because the temperature of the water causes the metal to be below the dew point of the atmosphere.

The paint was applied over three days and the vessel was returned to service after 24 hours. It was put back into service before the film properly cured.

In one week the tank showed blushings and a few blisters on the 24-hour dried film, some blushing on the 48-hour dried film and very slight blushing on 64-hour dried film.

Paper Stock At 160 F

Another tank coated inside with amine-cured epoxy and which contains a turbulent high density paper stock at 160 F developed some patch blistering after a year. This blistering is consistent with the minimum film thickness tolerance of the specification.

A second tank in this same service, but 15 F cooler, is in excellent condition after two years' service.

Criteria For Water Resistance

Based on experience amine-cured epoxy coatings are recommended for water resistance provided:

1. The coating system is formulated with the higher molecular weight epoxy resins and further plasticized to produce film density.
2. The reactivity of the converter and the solvent balance should be such that 100 percent conversion will be produced as quickly as possible after the solvent is completely released.
3. That paint systems be applied during seasons to take advantage of nature's baking system and that otherwise, heat should be used to catalyze the reaction.

It is desirable also to use the hot spray equipment because this accelerates the reaction and helps to dispel thinners. It is recommended also that a minimum of eight mils dry film thickness and an average of ten mils be used.

Sodium Sulfate Tank

A paper company in south Georgia had epoxies on test some seven years ago. These tests led to painting with epoxies a sodium sulfate storage tank that required recoating every 3 to 6 months. Because the environment was contaminated with caustic soda solutions, salt cake and included a salt air atmosphere, the corrosion rate was high. Coatings failed by saponification and because of thin films.

The tank was blasted and coated with five coats of amine-cured epoxy. These produced ten mils dry film whereas with other materials four to five mils had been obtained.

This same system was applied two years later to two new tanks some 50 feet from the older tank. When the first tank was inspected after five years, it showed 2 to 3 percent area film failure; but the newer two tanks each had large areas of failure. A film thickness gauge showed the areas failing had only two mils of film. The unaffected areas of the tanks showed a ten mil film.

Compensating For Poor Design

Back-to-back channel spaces are now being protected as follows: The channel

Epoxy Coatings—

irons are cleaned on the outside and along the accessible areas inside the channel space. The cleaned surfaces are primed with an amine-cured epoxy primer. This is allowed to dry for an hour or longer. An amine-cured fiberated epoxy is then worked into the channel space to a depth of one inch from both outside areas with a putty knife. This is allowed to dry overnight to produce a heavy skin over the epoxy caulking. After overnight drying epoxy finish coats are applied over the outside of the angle iron and over the caulking. This traps the solvents in the caulking which remains rubbery indefinitely. This procedure has been adopted because it seals the channel space from the environment and stifles corrosion in the areas enclosed by the caulking. Residual chemicals and moisture in this space react with the iron to form stable compounds and, when they are consumed, corrosion stops.

Protecting Structural Steel

Steel in a southern Alabama plant was sandblasted at the fabricators' shops. The cleaned steel was primed with a coat of the amine-cured epoxy and one finish coat in one to four hours after the primer was applied. The painted steel then was packed in freight cars using wood spacers. At the plant site the steel was erected carefully. Areas damaged in erecting received a spot coat of primer followed by two coats of an amine-cured epoxy finish coat in a few hours. This rapid recoating proved convenient to paint contractors because it enabled them to finish the job without moving scaffolding.

Out of thousands of repaint jobs investigated none failed due to poor adhesion between coats. One tank, for example, was recoated after five years with excellent results.

The fiberated amine-cured epoxies that

have appeared recently have unusual film building properties often producing 40 to 60 mils dry film thickness in three coats. Troweled applications have been made that range up to ¼-inch thick.

Positions Wanted

Corrosion Engineer—Five years' experience in design and follow-up of cathodic protection installations. Prefer pipe line company in South or Southwest. Reply CORROSION, Box 57-18.

Chemical Engineer—eight years' experience research, development, and technical service in chromium chemicals, metal finishing, corrosion control, and water treatment. Seeks responsible position in east coast area. CORROSION, Box 57-20.

Corrosion & Chemical Sales Engineer, presently employed in sales and service of industrial, municipal and federal accounts, desirous of change. CORROSION, Box 57 - 21.

Aggressive Young Man with seven years experience in industrial paint formulation and three years practical applications problems in organic corrosion resistant coatings, interested in technical, management, or tech service position. Reply CORROSION, Box 57-23.

Positions Available

Principal Corrosion Engineer: Study o the fundamentals of corrosion relating t ferrous metal in environmental media o liquid metals, aqueous solutions an gases. Applicant should be Ph.D. grad or 3 to 5 years experience in corrosion technology. Salary commensurate with ability. Located Western Pennsylvania Replies confidential. CORROSION Box 57-22.

Business Opportunities

Manufacturer's Agent—To handle established complete line corrosion resistant maintenance coatings, floor coverings and tank linings for industry. West Virginia and Washington-Oregon territories available. Prefer experience or related lines. Outstanding opportunity. Write CORROSION, Box 57 - 19.

George J. Haruch

George J. Haruch, Creole Petroleum Corp., Cabimas, Venezuela, was killed in an automobile accident May 19. He joined NACE in January, 1956.

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Controlling Corrosion of Textile Mill Air Conditioning Equipment*

Introduction

GROWING USE of air conditioning equipment in textile mills has focused attention on prevention of corrosion in these costly installations. This article relates some of the work done along these lines with some suggestions for future work.

A basic reason for the rapidly expanding use of air conditioning in textile mills is the fact that textile fibers can be processed best when their moisture content is definitely proportionate to that in the surrounding air. For warping, twisting and winding, most mills maintain relative humidities around 55 percent and temperatures of around 82 F. In the weave rooms, higher humidities usually are maintained. For most synthetics, 60-65 percent and for cotton 80-85 percent relative humidities are maintained. If the relative humidity becomes too low, the yarn becomes stiff and does not "run" properly and increasing difficulties with static electricity are encountered.

Personnel comfort is also important in the textile industry because the heavy motor loads cause temperatures to rise over 100 F during warm weather.

Types of Air Conditioning Equipment

A popular type known as the humiduct system draws in fresh air through a blower, exhausting this air through ports or ducts in the mill. In front of each port a spray nozzle controls the amount of moisture. Temperature is regulated by heating or cooling coils in a central location and instrument controls throughout the plant maintain the proper temperature and humidity. This type of equipment is used largely for spot conditioning and is considerably more expensive to install if a plant is to be wholly air conditioned.

More and more mills are using and installing the central station type of equipment which draws in fresh air and uses return air from the plant. The return air is laden with dirt, lint, fumes, etc. and the combination of fresh and return air is passed through baffles which eliminate much of the dirt and foreign material. It then passes through a room where a band of spray nozzles wash the air which then is drawn through another set of baffles into the central fan which will carry up to 500,-000 cfm per blower. The air is then passed through duct work to the various operating areas. Temperature and humidity controls are in the operating areas.

Corrosion discussed is limited here to the central station type of equipment.

Saturated Air Is Cause

Major cause of corrosion is the handling of saturated air in the washers and fans. The high impact of this satu-

Abstract

Operating conditions of air conditioning equipment in textile mills are described. Some design defects are pointed out and remedial measures suggested. A procedure related to available plant shut-down time for surface preparation and coating of central air conditioning systems is described in detail, together with some recommended coating systems. Vinyls and zinc rich paints are suggested as the best coatings available now for the application conditions prevailing.

rated air against the rotor, blades, housing, etc. with its contamination of lint, starch, size, etc., causes penetration of moisture and contaminants into crevices, cracks and pores. There is considerable abrasion.

The starches, water conditioners, sizes, etc. used are widely varied and should be studied carefully when protective measures are being considered. Most sizing solutions are neutral in the size box, but when combined with lint, adhere to various parts of the central station. When proper conditions exist, considerable bacteria growth takes place and produces a wide variation in pH, first to an acid condition of pH 2.5 and as the biochemical reaction continues, the pH will rise to about 11. The clinging lint also produces oxygen-poor areas on the steel with resultant accelerated corrosion at these points.

Certain operations in textile mills, such as bleaching and dyeing, require the use of extremely corrosive chemicals involving a wide variety of acids, alkalis, oxidizing agents, dyes, etc. and these must be considered in any protective system for cooling and exhaust equipment used in these locations.

Too frequently this equipment is fabricated with no thought to bimetallic corrosion and various types of steel, brass, aluminum, etc. are unwisely used together, causing galvanic corrosion. For example, aluminum baffles may be mounted in a carbon steel frame, using stainless steel nuts and bolts.

Another cause of corrosion occurs when the textile plant is located in an industrial atmosphere or located near the sea coast. These conditions accelerate normal corrosion rates.

Present Methods of Corrosion Control

Until recently, little thought has been given to control of corrosion in air conditioning equipment. Frequently, new equipment has been installed with no other finish than a factory applied prime coat. The factory applied finish may involve more than a prime coat but frequently is applied over an improperly prepared surface and without reference to the type of service involved.

Maintenance in a textile mill presents many problems because most mills operate on a three-shift basis at least five and usually six or seven days a week and close down only one week per year, traditionally the week of July 4. During the annual shutdown, all maintenance on machinery, buildings, etc. must be performed. A mill having two or three

central stations (and some have ten or twenty) will find it impossible to properly clean and coat more than two or three stations during a week's time.

Maintenance usually consists of minimum surface preparation using steam cleaning, power driven grinding tools, wire brushing or hand scraping. Steam cleaning seems to be the least satisfactory, due to the fact that it usually lifts old coatings but does not leave a clean surface. Hand scraping also is quite unsatisfactory for surface preparation. The life of most good coatings, including vinyls and Neoprenes, is seriously shortened by the above mentioned inadequate surface preparations.

Sandblasting has proved to be the best method of surface preparation for new and corroded steel. However, it must be considered that the maximum working time for one central station will be 48 hours. Consequently, although a white metal blast cannot be attained, good results have been obtained with a commercial blast. This time limit, therefore, rules out coatings for units already in service which require a white metal blast as surface preparation.

During the 48-hour period, it is necessary to block all air ducts, return air vents and other openings to prevent dust and sand from contaminating nearby intricate spinning and weaving machinery. The area to be coated must be completely sandblasted, involving usually one to two thousand square feet. This operation, including clean-up, requires from 12 to 36 hours depending on condition and size of the equipment.

The protective coating must be applied quickly, consequently the coating selected must be fast drying and successive coats must be applied rapidly.

Due to equipment design, it is impossible to use thermosetting coatings. However, properly applied Neoprene, vinyl, epoxy and chlorinated rubber coatings have been used successfully. The newer zinc rich paints appear to be performing well where chemicals, starches, etc. are not present, such as in carding and spinning operations. In weave rooms and dye houses, the zinc rich paints are excellent as primers to be followed by epoxy or chlorinated rubber coatings for chemical resistance. The zinc prime coat prevents undercutting and rust creepage effectively and increases the bond of the barrier coats. When coatings have been applied in this fashion, minimum annual maintenance should give good protection for at least four years.

The procedure described is the best for coating and maintenance but present practice includes application of all types of coating ranging from 20 weight motor oil, axle grease, various paints, to the finest vinyl and epoxy coating. With improper maintenance, life of rotors has been as short as three years and entire units may be replaced in three to ten years involving costs of $8000 to $50,000 per unit.

Controlling Corrosion—

(Continued From Page 147)

Proposed Methods for Corrosion Control

There are several avenues of approach to better corrosion control.

Improved design is important primarily to make maintenance easier. On some equipment there are no access hatches or doors to the fan for inspection and maintenance. The blades, intake cones and vanes usually are of lap joint construction which causes excessive corrosion between the layers of steel which cannot be cleaned and coated properly. Housings also are lap jointed, with bolted and riveted construction. If seams could be butt welded and ground smooth, or if lap joints could be welded closed and ground smooth they could be more easily cleaned and satisfactorily coated. As many bolts and rivets as possible should be eliminated since these are particularly susceptible to coating failure and corrosion.

Penthouses or small buildings that house the air conditioning equipment, as presently constructed, often do not allow replacement parts to be installed without knocking down a wall, for example, to install a new fan rotor. Also, if various parts of the central station could be removed, by installation of track, large doors, etc. cleaning and maintenance would be greatly simplified.

Better Systems Necessary

Finally, improved protective coating systems would be of great benefit. One important possibility is the metallizing of new equipment with zinc or aluminum, of at least 5 mils, with application of an inert seal coat. This work must be done prior to installation when the equipment is disassembled so everything is accessible for white metal blasting, metallizing and sealing.

It is necessary, even with this system, to use air curing or catalyzed coatings because it would be virtually impossible to cure thermosetting coatings at relatively high temperatures. When using metallized systems care must be taken not to throw wheels out of balance. Also, although the cost of this type of protection often is at least 100% higher than conventional coating systems, it is felt that metallizing should last indefinitely, provided the seal coat is maintained in good condition.

Of the protective coatings used to date, vinyls appear to give very dependable and long-lasting service with ease of application. Certain formulations have superior bonding qualities and give greater mil thickness per coat. However, this does not imply that other coatings such as epoxies, Neoprenes, phenolics and others cannot be used with equal success. As in other types of service, anchor pattern, degree of cleanliness and mil thickness are the most important factors to be considered.

The zinc rich paints appear, at this time, to offer the best solution to undercutting of corrosion. These, when overcoated with inert coatings should offer the most economical long range corrosion protection for cold spray applications.

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Subscribers to CORROSION are found in over 40 foreign countries.

CORROSION ABSTRACTS

3. CHARACTERISTIC CORROSION PHENOMENA

3.8 Miscellaneous Principles

3.8.3

Electrongraphic Investigation of the Nature of Passive Layers. (In Russian.) V. P. BATRAKOV AND I. A. PONIZOVSKAIA. *Bull. Acad. Sci. USSR* (Izvest. Akad. Nauk SSSR), Physical Series, **20**, No. 7, 830-833 (1956).   13512

3.8.4

Anomalous Electron Emission from Metallic Surfaces. F. R. BROTZEN. Naval Research Laboratory, April, 1956, 12 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 111938).

Heating and cooling tests on low-melting abraded metals and alloys were undertaken in an effort to determine why electrons are irregularly emitted from the metal surfaces at temperatures below those characteristic of thermionic emission. The solidification of tin, bismuth and cadmium were found to be associated with an anomalously high emission rate. Lead, lead-tin alloys and a cadmium-tin alloy had no emission peaks

during solidification. However, lead and a cadmium-tin alloy exhibited emission peaks during the heating cycle at temperatures below their melting points. Kramer's effect is reviewed and possible mechanisms are discussed. The emission phenomenon was felt to be associated with lattice imperfections migrating through the oxide film on the metal surface.   13535

3.8.4, 3.7.4

Chemical Aspects of Defect Structures in Solids. ALESSANDRO CIMINO. *Chim. e Ind.* (Milan), **38**, No. 3, 189-202 (1956).

Cimino discusses the principal types of defects in solids and their structural consequences. Frenkel and Schottky defects are explained; the relation between the number of equilibrium defects and energy is given; non-stoichiometry is illustrated by reference to FeO and TiO; among the solid solutions discussed are arsenic and gallium in germanium. An exposition of the energy states of a real solid starts with an ideal band model and shows the influence of defects on the energy states, with donor and acceptor impurities in germanium as examples; semi-conductivity is explained. The evidence that diffusion depends on defects is presented; solid-state reactions are mentioned. Solid-liquid reactions are illustrated by silver and sulfur; the factors governing the rate of solid-gas reactions are discussed, with reference to the formation of protective layers and the oxidation of alloys. The formation of nuclei of barium in the decomposition of $Ba(N_3)_2$ is discussed. Catalysis and adsorption are mentioned. 44 references. —MA.   13551

3.8.4

On the Structure of Thin Oxide Films on Single-Crystal Iron Films. (In German.) O. HAASE. *Z. Naturforsch.*, **11a**, 46-54 (1956) Jan.   13582

3.8.4, 6.3.8, 6.3.2, 6.3.14

Researches on the Oxidation of Metals and Alloys in the Fused State. I. Lead. II. Cadmium. III. Tin. IV. The System Tin-Lead. V. The System Lead-Cadmium. (In Italian.) PAOLO SPINEDI. *Gazz. Chim. Ital.*, **86**, Nos. 5, 6, 7, 561-608 (1956) May, June, July.

A study of the behavior in the solid or liquid state using a continuous recording thermogravimetric method. Graphic representation of the oxidation speed. Comparison with other work.—MR.   13656

3.8.4

Mechanism of Chemisorption: Hydrogen on Nickel. Part I. P. W. SELWOOD. *J. Am. Chem. Soc.*, **78**, 3893-3897 (1956) August 20.   13654

3.8.4, 6.3.6

Electron Diffraction and Microscope Study of the Surface Structure of Copper Single Crystals. (In English.) SUSUMU YOSHIDA. *J. Phys. Soc. Japan*, **11** No. 2, 129-139 (1956).

The submicroscopic structure of electrolytically polished and etched surfaces of copper single crystals was studied by electron diffraction and the electron microscope and by the light-figure technique. The etched surfaces are shown to be composed of submicroscopic facets belonging to the (100) zone, and the electropolished surfaces are smooth and undulating, the undulations being inclined at a small angle, ~4°, to the microscopic surface. The mean value of the internal potential of copper, derived from the undulations, is ~11 V., agreeing with the value 13.7 V. found by Tull [*Proc. Roy. Soc.*, Ser. A, **206** 232 (1951)]. 15 references.—MA.   13701

4. CORROSIVE ENVIRONMENTS

4.2 Atmospheric

4.2.1, 2.2.2, 3.6.6

Symposium on Atmospheric Corrosion of Non-Ferrous Metals. ASTM Special Technical Publication No. 175, May, 1956, 158 pp. American Society for Testing Materials, 1916 Race Street, Philadelphia 3, Pennsylvania.

Contents: W. H. Finkeldy, Introduction; H. R. Copson, Report of Subcommittee VI on Atmospheric Corrosion; C. J. Walton and William King, Resistance of Aluminum-Base Alloys to 20-Year Atmospheric Exposure; Fred M. Reinhart and George A. Ellinger, Effect of 20-Year Marine-Atmospheric Exposure of Some Aluminum Alloys; A. W. Tracy, Effect of Natural Atmospheres on Copper Alloys; 20-Year Test; D. H. Thompson, A. W. Tracy and John R. Freeman, Jr., The Atmospheric Corrosion of Copper: Results of 20-Year Tests; H. O. Teeple, Atmospheric Galvanic Corrosion of Magnesium Coupled to Other Metals; K. G. Compton and A. Mendizza, Galvanic-Couple Corrosion Studies by Means of the Threaded-Bolt-and-Wire Test; E. A. Anderson, The Atmospheric Corrosion of Rolled Zinc; George O. Hiers and Elbert J. Minarcik, The Use of Lead and Tin Outdoors; H. R. Copson, Atmospheric Corrosion Behavior of Some Nickel Alloys.—MA.   13493

4.2.3

Corrosion and Deposit Caused by Flue Gas in Firing Installations. (In Norwegian.) PER BERGAN. *Teknisk Ukeblad*, **104**, 81-87 (1957) Jan. 31.

Problems created by the presence of sulfur and mineral elements in fuels. The use of dolomite gave good results in the case of corrosion and deposits at high and low temperature.—BTR. 13768

4.2.3, 6.2.5, 3.5.9

Gas Corrosion of Austenitic Steels at High Temperatures. (In Russian.) E. A. DAVIDOVSKAIA AND L. P. KESTEL. *Metallovedenie i Obrabotka Metallov*, No. 10, 29-34 (1956) Oct.

Study of a series of heat-resistant alloy steels relative to gas turbine installations.—BTR.   13528

4.2.3, 7.1, 3.5.2

The Fouling of Turbine Blades by Fuel Ash. Pt. IV. Pressure Tests with Cambered Blades. J. J. MACFARLANE AND F. S. E. WHITCHER. Brit. Ministry of Supply, Nat'l. Gas Turbine Estab. Rept. No. R.193, July, 1956, 23 pp.

Description of a short series of rig tests to investigate ash deposition and corrosion on a cascade of cambered blades at pressures to 4 atmospheres absolute. Severe choking of cascade by low temperature deposits was demonstrated and conclusions are given concerning relationship between weight of deposit and cascade pressure drop. Tests at 700 C using Nimonic 80A blades confirmed existence of a maximum rate of corrosion at intermediate rates of deposition of vanadium pentoxide. Two special tests were carried out, using a Kuwait fuel oil of low vanadium content and suggestions are made concerning combustion problems raised by results. Graphs, tables, diagrams.—INCO.   13639

4.3 Chemicals, Inorganic

4.3.3, 6.2.5, 8.4.5

Attack of Circulating Aqueous-Thorium Dioxide Slurries on Stainless Steel Systems. D. G. THOMAS. Oak Ridge National Lab. U. S. Atomic Energy Comm. Pubn., CF-56-1-21, January 5, 1956 (Declassified November 2, 1956). 64 pp. Available from Office of Technical Services, Washington, D. C.

An analysis of the attack rate data obtained while operating the 100A loops S and T, with thorium oxide slurries is presented. Data from the literature on the attack rate of slurries are also presented which supplements the results from S and T loops. Attack rates for these specific systems and where possible, the relative contributions of different variables to the over-all attack rate were established. By establishing the trends and the relative importance of the different variables it should be possible to set the operating conditions for a slurry system to give a minimum attack rate. And if, as is entirely probable, conditions giving minimum attack rate are not those found most desirable to minimize the handling or caking problems, the attack rate for various compromise conditions can be estimated and the most satisfactory one chosen. (auth)—NSA.   13746

4.3.6

The Corrosion Resistance of Constructional Materials to Titanium Tetra-

chloride. F. L. BETT. *J. Australian Inst. Metals,* **1,** No. 1, 49 (1956) May.
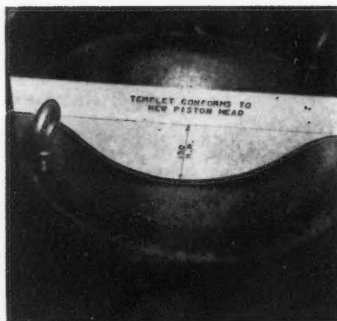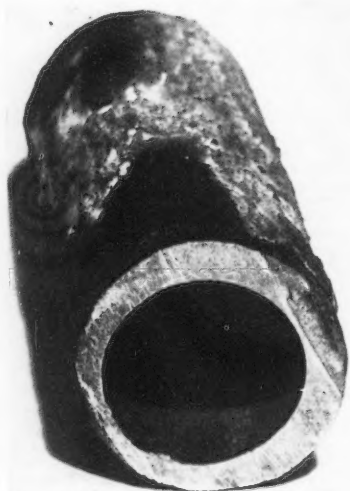
Tests on various materials in liquid and vapor titanium tetrachloride up to 500 C. At the boiling point (136.5 C) molybdenum, various stainless steels, Inconel, Monel, Nimonic 75, nickel, mild steel and cast iron lost no weight by corrosion (free-cutting steel, aluminum, aluminum bronze, manganese bronze and phosphor bronze all showed some loss). The first six mentioned also showed no loss at 320 C; at 400 C all showed loss except 18/8 stainless steel containing molybdenum; at 500 C all showed loss. —BNF. 13507

4.3.6, 6.4.2
Corrosion of Aluminum in Uranium Nitrate Solutions. V. H. TROUTNER. Hanford Atomic Products Operation. U. S. Atomic Energy Comm. Pubn., HW-42364, April 6, 1956, 4 pp. Available from Office of Technical Services, Washington, D. C.

The corrosion of aluminum in uranium nitrate solution has been shown in laboratory tests to be too severe to permit the use of aluminum for containing hot uranium nitrate solutions. A minimum corrosion penetration rate of 2 mils per day was observed with M-329 aluminum in 1% uranium nitrate hexahydrate in pH 2 aqueous solution at 100 C. (auth)—NSA. 13712

4.4 Chemicals, Organic

4.4.5
Chlorothene in Aerosols. J. W. BARBER. Paper before Chemical Specialties Mfrs'. Assn., 43rd Ann. Mtg., Washington, D. C., December 4, 1956. *Soap and Chem. Specialties,* **33,** No. 2, 99, 103, 105, 209 (1957) Feb.

Discusses physical properties of Chlorothene (methyl chloroform), its use as a vapor pressure depressant in aerosols, its effect on metals and fibers and aerosol formulations. Table shows corrosion in ipy of metals subjected to 50:50 Chlorothene: water and to Chlorothene containing 0.01 water at 70 F (data for Monel and Type 304 included). Recent aerosol can corrosion tests indicate that considerable dissolved water can be present in Chlorothene before hydrolysis or corrosion will become a problem.—INCO. 13749

4.4.7, 3.2.2, 7.1
Effect of Lubricant on Pitting Failure of Ball Bearings. F. T. BARWELL AND D. SCOTT. *Engineering,* **182,** 9-12 (1956) July. Experimental results for various fluids. —MR. 13500

4.6 Water and Steam

4.6.1, 6.2.3, 3.4.7, 3.4.6
Some Loop Experiments in NRX Reaction to Study the Corrosion of Mild Steel by Flowing Water at 90 F. G. M. ALLISON. Atomic Energy of Canada Ltd., Chalk River Project. November, 1956, 24 pp.

The water conditions necessary for minimum corrosion in the mild steel thermal shield recirculating systems in NRX and NRU were studied. The chemical and corrosion results obtained by operating three mild steel loops in which water at 85 to 95 F was recirculated through test sections located in J-rod positions in the NRX reactor are reported. Lowest corrosion rates were found when the

water was maintained at pH 10.5 with or without oxygen being present. In both cases the corrosion was general in nature and no pitting occurred. At pH 7 with oxygen present in the water severe pitting took place and the corrosion rate was several times higher than similar conditions without oxygen in the water. Under oxygen-free conditions the corrosion product was Fe_3O_4. At pH 7 and with 3 to 5 ppm of oxygen in the water the corrosion product was a mixture of Fe_3O_4 and $\gamma\text{-}Fe_2O_3$. At high pH with oxygen present Fe_3O_4 predominated with some traces of Fe_2O_3. The systems tested may be listed in order of increasing corrosiveness: high pH with or without oxygen in the water < water at pH 7 with no oxygen present and continual purification < water with no oxygen present and no purification or pH control < water at pH 7 with 3 to 5 ppm of oxygen present. (auth).—NSA. 13491

4.6.1, 3.4.7, 3.5.11
Effects of pH and Velocity on Corrosion of Steel Water Pipes. ROLF ELIASSEN. CLEMENTE FEREDA, AMILCAR J. ROMEO AND ROLF T. SKRINDE. *J. Am. Water Works Assoc.,* **48,** 1005-1018 (1956) August.

Past investigations, objectives of study, experimental apparatus, observed effect of pH, mechanism of pH effects, theoretical velocity effects.—MR. 13594

4.6.1, 6.6.7, 8.4.5
Exposure of Several Different Rubber Compounds to Pile Water. Irradiation Service Request HAPO-104 (Final Report on PT 105-505-SI, Supplement A). J. P. Cooke. Hanford Atomic Products Operation. U. S. Atomic Energy Comm. Pubn., HW-32428, Sept. 9, 1954 (Declassified Feb. 20, 1956), 13 pp. Available from Office of Technical Services, Washington, D. C.

A series of tests was made to evaluate the deterioration rates of various elastomers in active contact with pile effluent. The most promising compounds for use in γ fields and in pile effluents are listed.—NSA. 13556

4.6.2
Boiler Water Treatment: A General Review. T. H. TURNER. *Corrosion Prevention & Control,* **3,** No. 9, 37-40 (1956) Sept.

Reviews British Standards Specifications concerning boiler water treatment. Tables list typical analyses of waters used for locomotive boiler feed (1942) expressed as grains per Imperial gallon (parts per 70,000) and compositions of natural waters in Great Britain. Battersea Polytechnic has arranged for residential summer school on corrosion covering subject Water Treatment. BSI specifications covering boiler water for marine boilers and land boilers were conveniently summarized by the author in *The Engineer,* June 24, 1954.—INCO. 13728

4.6.2
The Uses of Amines in Combatting Corrosion in Condensate Systems. J. R. COURSAULT. Paper before Am. Pulp and Paper Inst., So. East. Sect., Greenville, S. C., Sept. 28-29, 1956. *Tappi,* **39,** No. 12, 155A-158A (1956) Dec.

Describes causes and characteristics of corrosion by oxygen and carbon dioxide in condensate return lines and methods for preventing attack. Oxygen is eliminated by effective mechanical and chemical (sodium sulfite, hydrazine) deaeration. Since carbon dioxide is

formed from bicarbonate alkalinity of feedwater, deaeration is not effective. If carbon dioxide concentration of steam is low, use of neutralizing amines (cyclohexylamine, morpholine) for raising pH of condensate may be proper choice. If carbon dioxide concentration in steam is in high range, use of filming amines (such as octadecylamine) is warranted.— INCO. 13559

5. PREVENTIVE MEASURES

5.3 Metallic Coatings

5.3.4
Improved Techniques for Electroless Nickel Plating on Nonconductors. H. NARCUS. Paper before Am. Electroplaters' Soc., 43rd Ann. Conv., Washington, D. C., June 17-22, 1956. *Tech. Proc. Am. Electroplaters' Soc.,* **1956,** 157-161.

Details for improved electroless nickel coatings on ceramics, glass, quartz and plastics, cover cleaning, roughening, sensitizing activation and electroless nickel bath. Sensitizing agent which gives more rapid coverage and adhesion than stannous chloride, is solution of stannous fluoborate concentrate, fluoboric acid, hydrofluoric acid and Triton NE. An activat-

ing solution of 0.01-0.1 grams auric chloride (50%) in 1000 cc water gives improved results over palladium chloride activating agent. Composition is given for bath which produces most consistent results. Experimental data confirming these improvements are given for electroless nickel on ceramic specimens. Tables.—INCO.   13259

5.3.4
Practical Aspects of Cadmium Plating. J. KOSMOS. *Plating,* 43, No. 10, 1235-1240 (1956) Oct.

Advantages of cadmium plating; recommended thicknesses for protection of steel; compositions of fluoborate and cyanide (still and barrel) plating solutions; plating procedure; addition agents; factors affecting throwing power; analysis for control of plating compositions (cadmium, sodium cyanide, sodium hydroxide, sodium carbonate).—BNF.
13166

5.3.4
Addition Agents in Nickel Plating. R. B. FISCHER AND C. E. RING. Indiana Univ. *Plating,* 43, No. 11, 1338-1341 (1956) Nov.

Investigation of certain phases of brightening mechanism of addition agents by isolating effects of all other conditions and components of plating bath. Addition agent, its concentration and nickel deposit thickness were varied systematically, whereas basis metal (copper), temperature, pH, current density, agitation and physical dimensions of apparatus were kept constant. Addition agents selected were 1, 5-naphthalene disulfonic acid and saccharin. Plating bath was low pH Watts type bath. Deposits were observed by specular and diffuse reflectivity measurements, x-ray diffraction, electron diffraction and electron microscopy.—INCO.   13171

5.3.4
The Mechanism of Deposition of Titanium Coatings from Fused Salt Baths. M. E. STRAUMANIS, S. T. SHIH AND A. W. SCHLECTEN. Univ. of Missouri. *J. Electrochem. Soc.,* 104, No. 1, 17-20 (1957) Jan.

Mechanism of titanizing process consists in direct collision of titanium particles dispersed in a molten salt bath with surface of metallic or ceramic object submerged. Titanium particles stick to surface and if temperature is high enough, a part of titanium deposited diffuses into substrate, forming a diffusion layer. Iron, low carbon steel, cobalt, nickel, noble metals and ceramic materials such as porcelain and Alundum are coated by this process. Coatings on iron are also produced in fused salts containing lower titanium chlorides in larger amounts but no metallic titanium. Collision and exchange mechanisms may go on simultaneously with more active metals. However, not more than 4.0% of total titanium coating is produced by latter mechanism. Lower titanium chlorides in fused salt baths are formed by reaction $Ti + 3NaCl \rightarrow TiCl_3 + 3Na$; the sodium evaporates partially at working temperature of above 900 C. Tables, 14 references.—INCO.   13469

5.3.4
Embrittling Effect of Molybdenum on Electrodeposited Copper: Tech. Note 363D. H. R. SKEWES. *J. Metals* (Trans. AIME), 9, No. 1, 192 (1957) Jan.

Extremely brittle copper deposits were obtained from electrolytes prepared by

leaching calcined chalcopyrite with aqueous sulfuric acid. Electrolytes were found to contain 10-25 g/l molybdenum. Importance of oxidation state of molybdenum was shown when molybdenum-containing electrolyte was continuously circulated through bed of fine copper metal; ductile deposit containing no molybdenum resulted.—INCO.   13152

5.3.4
Welding Composite Steels: Applied Liners. H. THIELSCH. Grinnell Co., Inc. *Machine Design,* 28, No. 28, 86-91 (1956) July 26.

Discusses fabrication of applied liners (composite plates of thin sheet of corrosion-resisting metal bonded intermittently to backing steel) by spot and seam welding and by arc welding techniques. Plug, strip and through welding methods are considered. Table lists electrode and welding-rod compositions ordinarily recommended for welding stainless steel, nickel and Monel to mild or low-alloy backing steels. Diagrams.—INCO.   12607

5.3.4, 4.7
The Attack of Iron-Containing Zinc Metals on Iron Containing Copper. (In German.) D. HORSTMANN. *Arch. Eisenhuttenw.,* 27, No. 4, 231-233 (1956) April.

Time and temperature dependence of attack by zinc saturated with iron, on iron with up to 0.91% copper. Structure and growth of iron-zinc alloy layers.—BNF.   13172

5.3.4, 6.3.9
High-Temperature Adherence of Nickel Plates to Molybdenum. S. S. BRENNER. *Plating,* 43, No. 9, 1143-1144 (1956) Sept.

Adherent nickel plates of up to 0.03 cm in thickness can be produced on molybdenum by use of a brass strike (-10^{-5} to 5×10^{-5} cm thick) and heat treatment (anneal at 750-900 C in oxidizing atmosphere). During heat treatment, zinc evaporates and islands of copper are formed. Nickel plate is held down by these islands so that sufficient diffusion welding between nickel and molybdenum can occur to prevent blistering and buckling. Photomicrographs.—INCO.   12754

5.4 Non-Metallic Coatings and Paints

5.4.2, 8.4.5
Report on National Bureau of Standards Ceramic Coatings on Inconel and Stainless Steel. R. E. TATE. Tennessee Eastman Corp. U. S. Atomic Energy Comm. Pubn., AECD-4073, July 2, 1945 (Declassified January 10, 1956), 13 pp. Available from Office of Technical Services, Washington, D. C.

Three types of coatings were tested in the alpha sublimation still and exposed to the ion beam of the M unit. It was found that these applications are too rigorous.—NSA.   13398

5.4.5
Corrosion Protection by Paint. B. WAESER *Deut. Farben-Z.,* 10, No. 3, 84-87 (1956).

A review of the electrochemical corrosion-inhibition theory and its application in practical protective systems, principally, e.g., in the use of pigments cathodic to the metal to be protected. Wash primers and zinc and aluminum

powder paints are considered as examples. The importance of moisture diffusion is also stressed and tables of water absorption and permeation are given for a number of media.—RPI.   13419

5.4.5
Lacquers and Paints in the Battle Against Corrosion. G. SPROCK. *Paintindia,* 6, No. 2, 26-31 (1956).

An account is given of anticorrosive paints, especially vinyl-resin-based types, their application and testing.—RPI 13358

5.4.5
Rust-Inhibitive Pigments. L. R. SHERMAN. *Official Digest Federation Paint and Varnish Production Clubs,* 28, No. 379, 645-662 (1956).

A comprehensive view of corrosion-inhibitive pigments and wash primers with eight references.—RPI.   13374

5.4.5
Protection against Rust with Special Reference to the New Anti-Rust Pigment Calcium Plumbate. B. SUPPAN. *Prakt. Chem.,* 7, 41-44 (1956); *J. Appl. Chem. Absts.,* 6, Pt. 7, ii-29 (1956).

A discussion is given of the mechanism of rusting of painted iron surface by the action of air and moisture (including air and moisture trapped in the crevices of the painted iron surfaces) and by the ensuing electrolytic action. The use of passivating coatings (phosphates, chromates, etc.) and their limitations are discussed and the desirable properties of paints for effective protection against rust are outlined. The advantages of calcium plumbate oil paints in this connection are shown.—RPI.
13427

5.4.5
Organic Protective Coatings for Metals: Their Assessment and Development in India. B. S. RAO, C. P. DE AND V. V. KELKAR. *Paintindia,* 6, No. 5, 23-26 (1956).

The role of organic coatings in protecting metals against atmospheric and underwater corrosion is reviewed. Both materials and methods in current use are discussed, with particular regard to the Indian economy. 12 references.—RPI.
13312

5.4.5
Painting of Castings. E. JOHNSON. *Electroplating & Metal Finishing,* 9, No. 7, 225-228 (1956).

The painting of castings presents some rather special problems and each job needs careful study to find the most economical method of trouble-free paint finishing. Most castings are of poor quality and production schedules often allow insufficient time for proper filling and rubbing down, while the size of many castings means that handling after cleaning often cannot be avoided, in addition to which there may be stoving difficulties. Spray application of filler is preferred to brush filling or knifing all over, as it is less likely to bridge cavities.—RPI.   13253

5.4.5
Epoxidation and Uses of Epoxides in Coatings. Pt. II. Plasticizers, Stabilizers and Mechanism of Their Action. DANIEL SWERN. *Paint and Varnish Production,* 46, 29-36, 99 (1956) May.

What plasticizers and stabilizers are, what they are expected to do, how they work, how they are evaluated and what the mechanism of their action is. Table. —MR.   12612

5.4.5

Vinylidene Chloride Resins. A Report of NACE Technical Unit Committee T-6A on Organic Coatings and Linings for Resistance to Chemical Corrosion. (R. McFarland, Chairman), Prepared by Task Group T-6A-3 on Vonylidene Chloride Polymers (R. L. Brown and S. F. Roth, Chairmen). *Corrosion,* **13,** No. 3, 211t-214t (1957) March.   13133

Vinylidene chloride resins can be formulated into coatings characterized by exceptional resistance to water fuels and gases. Resistance to acids, salt solutions and mild oxidizing agents is excellent to good while alkali resistance is fair to poor. The two commercially available forms of vinylidene chloride resins are the copolymers with vinyl chloride and acrylonitrile.

Recommendations are made regarding the use of vinylidene chloride coatings in various media including several acids, alkalis, oils, oxidizing agents, salts, solvents, gases and water. These recommendations were compiled from experience reports by a number of users.

Physical properties of vinylidene chloride resins are given. Application of coatings is discussed in detail with attention given to coverage and shipping data, flammability and toxicity, surface preparation, priming and application methods. Properties of applied coatings and linings are considered with respect to temperature limitations, impact and abrasion resistance, hardness, ageing, toxicity and odor, weight and electrical properties.   13133

5.4.5, 1.1, 1,2,2

Guarantee of Durability in the Efficiency of Protection by Multi-Coat Anti-Rust Systems. III. Economic and Social Aspects. H. Rabate. *Peintures, Pigments, Vernis,* **32,** No. 5, 417-418 (1956).

The preservation of structures is of economic and social importance and ought to be considered from the viewpoints of annual cost (not simply first cost) and expertness of execution. —RPI.   13316

5.4.5, 2.3.7, 5.4.6

Properties, Specifications, Tests and Recommendations for Coal Tar Coatings. Part II. Cold Applied Coatings. W. F. Fair, Jr. *Corrosion,* **12,** No. 12, 605t-610t (1956) Dec.

Principal characterists of cold applied coal tar coatings are considered with respect to applications. After reviewing the prerequisites of surface preparations, criteria for selection with respect to the exposure are considered. Five classes of coatings produced by one or more manufacturers are itemized and their general characteristics outlined. Care in selection of primer is emphasized and types of acceptable primers to be used under coal tar coatings mentioned.

After reviewing briefly the problem of water vapor permaebility the author discusses the theory of transmission and gives definitions of transmission rate, permeance and permeability. Methods whereby these characteristics may be evaluated with respect to a specific coating are given. Results of an investigation of vapor transmission rates for three classes and one system of coating are tabulated. Permeance of commonly used building materials is tabulated.

Recommended coal tar systems for

numerous exposures of piling, pipe and other metal structures are given.   12647

5.4.5, 4.2.1

Protective Coating for Atmospheric Use: Their Surface Preparation and Application Requirements, Physical Characterisics and Resistances. A Preliminary Report by NACE Technical Unit Committee T-6B on Protective Coatings for Resistance to Atmospheric Corrosion (L. L. Sline, Chairman). *Corrosion,* **13,** No. 3, 215t-223t (1957) March.

Detailed information is given on the application requirements, physical characteristics and resistances of 22 different types of binders. Materials discussed include drying oil paints, ester gum-oil, straight phenolic oil varnish, modified phenolic oil varnish, straight alkyd varnish, modified alkyd varnish, epoxies, chlorinated rubber, vinyls, metallic silicate (zinc loaded), six coal tar coatings and five asphalt coatings. Information pertaining to the following points is given for each material: recommended surface preparation, number of coats, approximate dried film thickness of each coat, approximate air-drying time before recoating, usual method of application, application surface temperature, thinners, general flammability classifications, compatibility with other types, abrasion resistance, gloss retention, resistance to petroleum oil and grease, maximum temperature limitations, approximate storage life under normal conditions and health hazards.

The information given pertains primarily to the use of coatings for the protection of steel as used in bridges, tanks, towers, fences and railroad cars exposed to rural, industrial and marine atmospheres. Data given are not applicable for strongly corrosive chemical or marine atmospheres.   13129

5.4.5, 4.2.4

Painting of Steel Structures in Industrial Atmospheres. I. V. Tolvanen. Teknillisen Kemian Aikakauslehti (*Technical Review*), **13,** No. 5, 139 + 3 pp. (1956).

Corrosion inhibition by the action of red lead, lead cyanamide, zinc chrome and zinc tetroxychromate in anticorrosive paints in discussed. Paint application, surface preparation, pretreatments, actual painting and the requirements to be met by surrounding influences when paint is being applied in industrial areas, are considered. —BTR.   13401

5.4.5, 5.4.10, 2.2.6

Testing of Coal Tar Coatings. Part II. Field Exposure in Cold Climates. W. F. Fair, Jr., C. U. Pittman and M. G. Sturrock. *Corrosion,* **13,** No. 3, 191t-194t (1957) March.

Details of an experiment are given in which 10-foot lengths of pipe were buried in Canada at depths of 1 through 5 feet after application of five systems of coatings and wrappings on groups of 5 pipes each. Pipes were buried after testing with an electronic holiday detector with self-registering thermometers in two pipes at each level. After a year's exposure the pipes were unearthed and tested electrically for holidays. Only a limited number of holidays were found and they were not apparently related in any way to the kind of coating or severity of exposure. Temperatures registered ranged from 25F to 34F increasing with depth.

Another test of pipes exposed to atmosphere but protected from the ele-

ments was made. Results after a year showed that although temperatures of —8F had been reached, holidays were few except in sections unwrapped but coated with unplasticized enamel. The advantage of wrapping in protecting the coating were obvious.   13149

5.4.7

The Powder Cold Spraying Method. (In German.) Hans Reininger. *Werkstoffe u. Korrosion,* **7,** No. 8/9, 452-460 (1956) August/September.

This process consists in simultaneously spraying from a twin-nozzle gun (a) solid material in powder form and (b) a solution of a binder (4% solids on powders). The solids may be a metal, glass, cork, asbestos, rubber, etc., and the binder amine-cured epoxy resins, silicones, some inorganic binders such as water glass and tar for water-resistant structures. Smooth metal surfaces must be roughened; a first coat of sprayed zinc is advantageous. The properties of the coating may be varied over a wide range. Results of practical corrosion tests are discussed. —RPI.   13343

5.4.10

Polyvinylidene Chloride Film and Microcrystalline Wax for Protecting Underground Pipe. Ted Kennedy, Jr. *Corrosion,* **13,** No. 3, 186t-190t (1957) March.

Six case histories are given of the use of polyvinylidene chloride film in conjunction with microcrystalline wax to protect underground pipes. It was found that microcrystalline wax of high quality appears to be a superior wetting agent and when wrapped with a protective film of polyvinylidene chloride will thoroughly and permanently protect a pipe surface from corrosion where properly applied. Although further information must be accumulated to substantiate fully the performance of these materials in the field, results to date indicate that these materials provide superior protection.   13135

5.6 Packaging

5.6.1

Corrosion Prevention in Packing and During Storage (In French.) F. Vandervelden and M. Pourbaix. Centre Belge d'Etude de la Corrosion, Rapport Technique No. 37, May, 1956, 3-8.

Various cleaning and drying methods for metallic parts before packing or storing. Coating processes and packing materials. —MR.   13416

5.6.1, 2.3.4

Corrosivity of Packaging Materials. E. Wallenberg and B. Jarnhall. *Modern Packaging,* **29,** 163 + 9 pages (1956) May.

A method of quickly determining the electrolyte content of a packaging material as an index of the material's corroding properties. Diagram, photographs, graphs, tables. 11 references. —BTR.   12640

5.6.1, 5.5.3

Temporary Protection of Metallic Surfaces Against Atmospheric Corrosion. N. Plavsic. *Zastita Materijala,* **4,** No. 3, 69-75 (1956).

The article gives a summary of agents

for the temporary protection of metallic materials against corrosion. The agents are divided in two groups—those which have a true anticorrosive effect and those which act merely by forming an impermeable coating. Each agent is described in detail and its good and bad properties are analyzed. Special attention is given to vaporphase inhibitors. —RPI.   13329

5.8 Inhibitors and Passivators

5.8.3, 3.6.8

The Influence of Polar Organic Substances and Catalytic Poisons on Hydrogen Overvoltage on Nickel and Iron Cathodes. (In English.) W. PALCZEWSKA. *Bull. Acad. Polon. Sci.*, Classe iii, 4, No. 1, 37-42 (1956).

From the shape of the polarization curves and observations of hydrogen bubbles on nickel and iron cathodes, it is establishen that in sulfuric acid containing 20-30 mg/l dibenzylsulfoxide, this is absorbed on nickel at a cathodic potential of —0.65 to —0.75 V and on iron at —0.7 to —0.8 V. With 100 mg/1 arsenous oxide also in solution, the sulfoxide is adsorbed on nickel and iron cathodes at —0.6 and —0.7 V, respectively. 7 references. —MA.   13313

5.8.3, 6.2.3

The Passivity of Steel in Nitrous Vitriol. E. I. LITVINOVA. *J. Applied Chem., USSR* (Zhur. Priklad. Khim.), 29, No. 10, 1521-1529 (1956).

The passivation of steel in nitrous vitriol was found due not to the formation of oxidic or other films but to the deposition of a dense coating of trivalent iron sulfate. Optimum results were obtained at about 100°. 5 tables, 3 figures, 10 references.—ATS. Translation available: Associated Technical Services, P. O. Box 271, East Orange, New Jersey.   13173

5.8.1

Corrosion Protection by Means of Inhibitors. (In Dutch.) M. OUDEMAN. *Metalen*, 11, No. 14, 304-309 (1956) July 31.

The mechanism of corrosion and the effects produced by anodic, cathodic or absorption inhibitors. A survey of various new practical applications. —MR.   13307

5.8.3

The Inhibition of Corrosion by Sodium Benzoate. J. H. KASER. *Corrosion Prevention & Control*, 3, No. 11, 37-40, 46 (1956) November.

Discussion of theory of corrosion and common methods of inhibiting corrosion. Results of experimental work that led to discovery and development of sodium benzoate for this use are summarized and theory of mechanism of such inhibition is considered in the light of more recent research. —INCO.   13153

5.8.3

How Corrosion Inhibitors Work. P. D. MUIR. Paper before Univ. Okla. Corrosion Control Short Course, Norman, April 3-5, 1956. *Petroleum Engr.*, 28, No. 12, B27-B29 (1956) Nov.

Several theories regarding manner in which inhibitors function are discussed. In many inhibitors, a general adsorption, cathodic and anodic adsorption, chemisorption and physical desorption and preferential oil wetting probably all combine to provide corrosion protection. These mechanisms can reinforce each other and in most inhibitor applications, it is believed that more than one mechanism is involved. Diagram.—INCO.   13305

5.8.3

The Effect of Some Corrosion Inhibitors and Activators on the Hydrogen Overpotential at Iron Cathodes in Sodium Hydroxide Solutions. I. A. AMMAR AND S. A. AWAD. *J. Phys. Chem.*, 60, 871-874 (1956) July.

Measurements were made in 0.2 N sodium hydroxide solutions to which organic substances were added. —BTR.   12744

5,8,3, 2.3.4

Researches on Corrosion and Inhibition. Reaction Velocity in the System Iron: Dilute Acetic Acid at 40C. G. S. GARDNER, H. L. FAIGEN, G. L. GIBSON AND W. S. HALL. Am. Chemical Paint Co. *J. Franklin Inst.*, 262, Nos. 5, 6, 369-384, 469-478 (1956) Nov., Dec.

Rate-determining factors in corrosion reactions are reviewed in light of work by Nernst, Langmuir and others and characteristics of diffusion and activation control in such reactions are discussed. Corrosion inhibitors are assumed to act by adsorption on metal surface. Rate equations containing the function s, the frictional surface covered by adsorbed inhibitor, express reaction velocity in diffusion and activation controlled systems. Equipment and procedure for studying velocity of corrosion reactions are discussed. Study of system iron:acetic acid at 40C with 1000 ppm acetic acid in absence of oxygen is made. Effects of two corrosion inhibitors are investigated. Results or plotted according to velocity equation for diffusion-controlled reactions. Value of s is calculated for each experiment; s is shown to be useful concept in corrosion testing to express inhibitor efficiency. Experiments in presence of an oil phase are discussed. Results cast some light on adsorption and water displacing theories of inhibitor action in oil wells. —INCO.   13217

5.9 Surface Treatment

5.9.4

Phosphatization a n d Anticorrosion. (In French.) ROGER LAGRADE. *Corrosion et Anticorrosion*, 4, No. 8, 289-296 (1956) Sept.

The principle of anticorrosive phosphatization, the deep and light processes, types of coating and application of the principle to non-ferrous metals.—BTR.   13258

5.9.4

**Oxidising and Phosphating Practice
in the USSR.** H. A. HOLDEN. *Electro-
plating and Metal Finishing,* **9,** No. 9,
291-292 (1956) Sept.

Recent information suggests that,
with one exception, Russian practice in
oxidizing and phosphating follows very
much along the lines of British and
American practice, while the fields of
application for the processes are also
similar. However, a combined oxide/
phosphate treatment for iron and steel
is also in use and is very interesting
in that it appears to combine the ad-
vantages of both types of process with-
out the disadvantages of either. The
solution uses a relatively low concentra-
tion of readily available material at a
temperature of 100 C and the coatings
are of fair corrosion resistance and dif-
ficult to remove mechanically. Details
are given.—RPI.   13237

5.9.4

Phosphatising. L. A. R. FELIPE. Inst.
y Acero, **9,** 92-99 (1956); *Chem. Absts.,*
50, No. 9, 6275h (1956).

The factors which affect the grain
growth of phosphatized layers on steel
have been studied. Experiments were
made on the zinc phosphate bath and
the manganese-base bath. The latter is
easier to use; the zinc bath must be
more carefully controlled.—RPI.   13210

5.9.4

**Phosphating of Aluminium and Alu-
minium Alloys.** O. KORELIC. *Zastita Ma-
terijala* **4,** No. 8, 258-259 (1956).

The chemical process of the anticor-
rosive protection of aluminum and its
alloys in solutions containing PO_4^{3-},
CrO_4^{2-} and F^- ions was investigated.
Formation of the protective coating is
influenced by the amount of F^- ions
present, temperature of the bath and
duration of treatment. The anticorrosive
action of protective coatings deposited
on aluminum, Peraluman and Dural was
investigated by laboratory methods and
found to be very effective.—RPI. 13163

5.9.4

**Colored Anodic Coatings on Alumi-
num.** H. BENGSTON. *Plating,* **43,** No. 7,
918-921 (1956) July.

Selection of dyes and pigments; multi-
color processes; effect of alloying ele-
ments, surface preparation and anodiz-
ing procedure, etc.—BNF.   12730

5.9.4, 2.3.9

**Structure and Crystallization of
Nearly Amorphous Beryllium Oxide and
Aluminum Oxide Films.** I. S. KERR. *Acta
Crystallographica,* **9,** Pt. II, 879-885
(1956) Nov. 10.

Two methods of preparing beryllium
oxide films suitable for electron-diffrac-
tion examination are described. These
films gave a halo diffraction pattern dif-
fering appreciably from that correspond-
ing to a broadened ring pattern from
normal hexagonal beryllium oxide. The
crystallization of this form of the oxide
was shown to occur at 300 C by heating
in air. Calculation showed that the halo
pattern originated from diffraction by
beryllium oxide crystals of normal
structure, but the crystals were only
8 A in diameter. The oxide film par-
tially stripped from anodized aluminum
was examined by electron diffraction
and haloes were obtained similar to

those reported previously. This film was
found to crystallize into γ-Al_2O_3 after
heating to 700 C for seven hours in air.
The possible structure of the nearly
amorphous oxide is discussed and the
model suggested by Wilsdorf is shown
to be likely. (auth).—ALL.   13159

5.9.4, 5.3.2

**Anticorrosion Treatment of Zinc
Coatings.** N. A. SOLOV'EV. *J. Applied
Chem., USSR* (Zhur. Priklad. Khim).
29, No. 7, 1062-1066 (1956).

Corrosion resistance of zinc coatings
was improved by a factor of 8-10 by
treatment in chromic, sulfuric and hy-
drochloric acids. 1 table, 5 figures, 4
references.—ATS. Translation available:
Associated Technical Services, P. O.
Box 271, East Orange, New Jersey.
                                             12615

5.9.4, 6.3.15

Conversion Coatings for Titanium. P.
D. MILLER, R. A. JEFFERYS AND H. A.
PRAY. *Metal Progress,* **69,** No. 5, 61-64
(1956).

Anti-galling surface coatings can be
produced on titanium alloys by anodic
oxidation in 5% sodium hydroxide solu-
tion at 205 F (95 C) with a current
density of 50 amp./ft.^{2} and by immer-
sion in the following solution: (a)
$Na_3PO_4 \cdot 12H_2O$ 50, $KF \cdot 2H_2O$ 20, 50%
HF 11.5 g./1. at 185 F (85 C) for 10
min.; (b) $Na_3PO_4 \cdot 12H_2O$ 50, $KF \cdot 2H_2O$
20, 50% HF 26 g./1. at 80 F (25 C) for
1-2 min.; or (c) $Na_2B_4O_7 \cdot 10H_2O$ 40, $KF \cdot$
$2H_2O$ 18, 50% HF 16 g./1. at 185 F for
20 min. The stated immersion times
yield maximum weight of coating. Re-
sults of various wear tests and of wire-
and tube-drawing tests show that ap-
plication of the coatings gave resistance
to seizure. A further improvement was
obtained when coated specimens were
heated in air at 800 F (425 C) for 1-5
hr. and it was concluded that increased
wear-resistance was conferred by the
formation of a layer of titanium dioxide.
The coating facilitated lubrication by
resin-bonded molybdenum disilicide.—
MA.   13267

5.9.4, 6.3.15, 4.3.2

**Protective Value of Oxide Films
Formed on Titanium Against Hydro-
chloric Acid.** (In English.) RIKURO
OTSUKA. *J. Japan Inst. Metals,* **20,** No. 1,
9-11 (1956).

Specimens of titanium sheet prepared
from sponge produced by the Kroll
process were subjected to various sur-
face-oxidation treatments and tested for
corrosion - resistance by immersion in
different concentrations of hydrochloric
acid at room and boiling point tempera-
tures. Boiling in concentrated nitric acid
renders titanium completely resistant to
24% hydrochloric acid at room tempera-
ture. Titanium becomes resistant to
100% hydrochloric acid at room tem-
perature after boiling in acid potassium
permanganate solution or a solution of
potassium chromate in sulfuric acid, or
after heating in air at 400-600 C. None
of these treatments; however, is effective
against boiling hydrochloric acid.—MA.
                                             13315

5.9.4, 6.3.20

**Variation of Anodic - Film Growth
with Grain Orientation in Zirconium.**
R. D. MISCH AND E. S. FISHER. *Acta
Metallurgica,* **4,** No. 2, 222-223 (1956)
March.

A letter. Grains in zirconium anod-

ized in 70% nitric acid showed varying growth rates of a black film which are dependent on the orientation of the grains. The rate is low when the anodizing plane is close to the basal plane, high when at 40 degrees to it, and low again at higher angles.—MA. 13300

5.9.4, 6.4.2

Low Valent Aluminum as a Product of Anodic Oxidation in Aqueous Solution. E. Raijola and A. W. Davidson, *J. Am. Chem. Soc.,* 78, 556-559 (1956) Feb 5. —BL. 13322

5.9.4, 6.4.3

Unipositive Beryllium as a Product of Oxidation. Barbara D. Laughlin, Jacob Kleinberg and Arthur W. Davidson. *J. Am. Chem. Soc.,* 78, No. 3, 559-516 (1956).

The anodic behavior of beryllium in aqueous sodium chloride solution indicates that the metal is oxidized anodically to a mixture of uni-and dipositive states.—MA. 13158

6. MATERIALS OF CONSTRUCTION

6.2 Ferrous Metals and Alloys

6.2.3, 8.4.2, 7.5.4

Protection of Structural Steel: The Preservation of Steel on Gas Works. L. A. Ravald. *Chemistry and Industry,* No. 48, 1526-1535 (1956) Nov. 26.

The author first discusses various ways of pretreating steel before a protective system is applied. Millscale may be removed by weathering and other foreign matter by mechanical tools, sand or grit blasting, flame-cleaning and rust removing solutions. Alternatively, the steel may be descaled and then hot galvanized or sprayed with zinc or aluminum. After briefly considering metal coatings, the author discusses paint systems for ordinary outdoor exposure and hot and humid conditions and gives examples of particularly corrosive influences. These include spray from coke-quenching shafts, condensates from crude coal gas and ammonia liquor and aerated water in cooling systems. Finally, the comparative life and cost of various pretreatments and protective schemes for gasholders are given. A sprayed zinc coating followed by a paint system lasts longest and is the most economical.— ZDA. 13319

6.2.5

Performance of Stainless Steel Sandwich Construction at High Temperatures. V. C. Setterholm and E. W. Kaenzie. Forest Products Lab., Dept. Agriculture. U. S. Wright Air Development Center, Tech. Rept. No. 55-417, Sept., 1956, 32 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (Order PB 121681).

High temperature performance of Type 321 and 17-7PH sandwich structures supplied by J. J. Foster Co., Goodyear Aircraft, Convair, Glenn L. Martin, Solar Aircraft and Twigg Inds. was evaluated. Edgewise-compression and flexure tests of sandwich constructions were conducted after specimens were heated at 75, 800, 1000 and 1200 F for 10 minutes and for 192 hours. Shear tests of sandwich constructions and core material (Type 321 and 17-7 PH) were made at room temperature. Materials were nickel, copper and silver brazed. Although many panels were corroded and poorly bonded, results of edgewise compression tests showed that specimens from panels weighing only 2.2 lb. sq. ft. can sustain facing stresses as high as 230,000 psi at 75 F and 57,000 psi at 1200 F. Description is given of test apparatus and results are discussed. Tables, graphs.—INCO. 13357

6.2.5

Know Stainless Steels When Selecting for Equipment. W. E. McFee. Armco Steel Corp. *Ind. & Eng. Chem.,* 48, No. 11, 1964-1970 (1956) Nov.

Discussion of stainless Types 300 and 400 and effect of content of chromium, nickel and other elements on corrosion resistance and mechanical properties. Resistance of stainless to atmospheric, general chemical, pitting, galvanic, crevice, stress corrosion cracking and intergranular corrosion is described with tests. Discussion of galvanic attack includes reference to Monel and Inconel. Importance of cleaning and passivation in applications of stainless steel is discussed. Graph shows effect of temperature and concentration of sulfuric acid and hydrochloric acid on corrosion of Type 316. Photomicrographs, diagram.—INCO. 13297

6.2.5

Stainless Steel for Pressure Vessels. A. Grodner. Continental Copper & Steel Inds., Inc. *Welding Res. Council Bull. Series,* No. 31, 1-20 (1956) Nov.

Stainless steels are used in pressure vessel construction to meet increasingly severe demands of modern processing industries because of their increased

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corrosion resistance, elimination of prod-
uce contamination, higher strength at
elevated temperatures, improved resist-
ance to scaling, improved toughness or
impact resistance at very low tempera-
tures and reduced maintenance costs.
Discussion of 35 grades of stainless
steels as to mechanical and physical
properties, corrosion resistance, embrit-
tlement phenomena, fabrication and weld-
ing is given. Photos, tables, graphs, 16
references.—INCO.   13224

6.2.5, 3.2.2
**Influence of Condition of Surface and
Structure of Stainless Steels on Their
Electrochemical Properties.** H. HATWELL.
Rev. Met., **53,** 729-735 (1956) Oct.
Role of oxygen adsorbed at the sur-
face of chromium-iron alloys in passiv-
ity phenomena. Selective corrosion in
stainless steels is discussed with sup-
porting data on 18/8, 25/20 and 18/8/Mo.
Metallographic and electron microscopic
study of intercrystalline corrosion in
these steels was made. A new type of
selective corrosion in stainless steels,
termed "honeycomb" corrosion, is de-
scribed. Effect of heat-treatment on this
selective corrosion is discussed.—INCO.
13227

6.2.5, 3.5.8
**Stress Corrosion Cracking in Type
403 Stainless Steel (Period covered
March 1, 1955 to April 30, 1956).** MARS
G. FONTANA. Ohio State Univ. Research
Foundation, Columbus. U. S. Wright
Air Development Center, Tech. Rept.
56-242, August, 1956, 58 pp. Available
from Office of Technical Services,
Washington, D. C. (Order PB 121414).
The effect of austenitizing tempera-
ture on the hardness, impact strength,
and microstructure of Types 403, 420
and 431 stainless steel was determined.
The optimum combination of these
properties occurred with austenitizing
temperatures of 1725, 1850 and 1900 F,
respectively for the 403, 420, and 431 ma-
terials. Tempered structures displayed
minimums in the impact strength, tem-
pering temperature curves at 1000, 900 and
1000 F for the 403, 420 and 431 materials
respectively. Metallographic studies were
made of stress-corrosion specimens tested
in a 1:1 hydrochloric acid and water
solution containing 1% selenium dioxide.
These studies showed that pitting was
initiated at manganous sulfide inclusions
and that cracking was associated with
the pits. Also, pitting characteristics
were dependent on tempering tempera-
tures and therefore are related to the
microstructure of the alloy. Cracking
does not occur in the Type 403 alloy
when it is tempered at 1050 F or higher.
This temperature is lowered to 900 F for
the Type 420 material and it is less than
700 F for Type 431 stainless steel
stressed to 75,000 psi and tested in the
above solution. Electron microscopy and
diffraction studies were made of tem-
pered Type 403 stainless steel. These
studies indicate several carbides to be
present in the alloy after tempering in
the 1000 to 1200 F temperature range.
Diffraction patterns vary for specimens
tempered in this range. (auth)—NSA.
13213

6.3 Non-Ferrous Metals
     and Alloys—Heavy

6.3.15
**Kinetics of the Reactions of Commer-
cially-Pure Titanium and Titanium Al-
loys with Oxygen, Nitrogen and Hydro-
gen. Part I. Desorption of Hydrogen**

from Commercially-Pure Titanium.
(In Japanese.) HIDETAKE KUSAMICHI,
YOSHIRO YAGI, TORU YUKAWA AND TADAO
NODA. *J. Japan Inst. Metals,* **20,** No. 1,
39-41 (1956).
An ingot obtained by arc-melting
sponge titanium using consumable elec-
trodes was forged into rod and annealed
at 700 C. Specimens of different
sizes were degassed in vaccuo (10^{-4}mm.
Hg) at temperatures of 700, 750, 800, 850
and 900 C, the evolved hydrogen being
collected and measured. A linear re-
lationship was found for log. concen-
tration hydrogen/temperature, enabling
the diffusion coefficient D to be calcu-
lated from Demarez's formula. The dif-
fusion coefficent for α-titanium, Dα, is
given by: $D\alpha = 0.27 \times 10^{-2} \exp(-14,200/RT)$.
The slight discrepancy between this
value and that obtained by Wasilewski
and Kehl [*Metallurgia,* **50,** 225 (1954)] is

attributed to impurities in commercially-
pure titanium.—MA.   13155

6.3.15
**A Study of the Tensile and Creep-
Rupture Properties of Fifteen Heats of
C-110M Titanium Alloy Sheet.** F. J.
GILLIG AND G. J. GUARNIERI. Cornell
Aeronautical Lab. U. S. Wright Air De-
velopment Center, Tech. Rept. 55-164,
January, 1956, 61 pp.
Fifteen heats of titanium alloy of
RC-130-A (c110-M) were tested at room
and elevated temperatures. Data were
analyzed for reproducibility and re-
lationships between room temperature
and high temperature properties at 500
and 700 F. Results indicate that a corre-
lation exists between room temperature
strength properties and yield and ulti-
mate strengths at 500 and 700 F. How-
ever, creep and rupture properties appear

to be independent of short time tensile strength results even at 700 F, which was temperature used for creep testing. Tables, graphs.—INCO. 13233

6.3.15
The Behaviour of Titanium at Elevated Temperatures. H. R. OGDEN. New York University Titanium Metallurgy Course, Lecture No. 14, Sept., 1956, 43 pp.

A survey with numerous useful graphs (17 references). Effect of alloying elements, creep and stress rupture, elastic modulus, thermal expansion, fatigue, thermal stability (including oxygen and hydrogen contamination), oxidation. Author concludes that tatanium and titanium alloys meet requirements of structural applications at 427-538 C; in the annealed condition are as good on a strength-weight basis as the very high-strength heat-treated steels; and will surpass the latter with the advent of heat treatments for higher strength of titanium alloys.—BNF. 13335

6.3.15
Changes of Mechanical Properties and Micro Structures of Commercially Pure Titanium Sheets by Cold Rolling and Annealing. (In Japanese.) Y. KONDO AND S. SUZUKI. *Sumitomo Metals*, **8**, No. 3, 26-47 (1956) July.

Ingot hardness of titanium ranged from 97 to 282 BHN, mainly because of differences in oxygen content, effect of degree of reduction, speed of tensile testing and temperature and time of stress relieving. Data given for hardness, tensile strength and elongation. Tensile properties were measured at various angles to the direction of rolling. Graphs show the UTS and elongation of cold rolled and of annealed commercially-pure titanium sheets over the temperature range of 0 to 800 C.—BNF. 13164

6.3.15, 3.2.2
Failures in Titanium Parts: Effects of Hydrogen in Commercial Alloys. H. D. KESSLER, R. G. SHERMAN AND J. F. SULLIVAN. *Metal Industry*, **88**, No. 3, 47-48 (1956) January 20.—BNF. 13180

6.3.15, 3.2.2
Effect of Hydrogen on Alpha Titanium Alloys. G. A. LENNING, J. W. SPRETNAK AND R. I. JAFFEE. *J. Metals* (Trans. AIME), **8**, No. 10, Sec. 2, 1235-1240 (1956) October.

Effect of 200 ppm hydrogen on microstructure and mechanical properties of iodide-titanium-based titanium-0.2% oxygen, -0.2% nitrogen, -10% tin, -5% aluminum and -5% aluminum-0.2% oxygen. Increase of hydrogen content precipitated a hydride phase and decreased notch-bend impact strength of alloys with oxygen, nitrogen or tin, similar to hydrogen embrittlement of high-purity titanium. In titanium-5% aluminum no hydride precipitation or embrittlement was found up to 180 ppm hydrogen.—BNF. 13167

6.3.15, 3.2.3
The Oxidation of Titanium. (In German.) PER KOFSTAD AND KARL HAUFFE. *Werkstoffe u. Korrosion*, **7**, No. 11, 642-649 (1956) Nov.

Temperature-time relationships are established for the reaction.—MR. 13246

6.3.15, 3.5.9
Titanium-36% Aluminum as a Base for High Temperature Alloys. J. B. McANDREW AND H. D. KESSLER. *J. Metals* (Trans. AIME), **8**, No. 10, Sec. 2, 1348-1353 (1956) October.

Oxidation resistance, stress rupture strength, creep and impact value of titanium-36% aluminum up to 1000 C (also with chromium and zirconium additions). It is thought to be an excellent base from which to develop more complex alloys of low density for superior performance from 800 possibly up to 1200 C. Scaling may be minimized by addition of niobium or tantalum.—BNF. 13296

6.3.15, 3.7.3
The Combined Effects of Carbon, Oxygen, Nitrogen and Hydrogen on the Properties of Titanium Sheet Weldments. J. F. RUDY. U. S. Wright Air Development Center, June, 1956, 44 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 121491).

The results of various destructive tests illustrate how the physical properties of welded and unwelded titanium are affected when prepared with the interstitial contaminants carbon, oxygen, nitrogen and hydrogen at low, medium and high levels. Thirteen alloys in ⅛-inch sheets were arc welded. Physical properties were determined by bend, tensile and impact tests, hardness measurements and metallographic observations. The resulting data provide aid in determining the maximum allowable combined percentages of interstitial contaminants that may be used with weldable titanium. 1337.

6.3.17
Autoclave Tests of Tuballoy (Uranium) Slugs and Alloys. N. BENSON, R. P. STRAETZ AND J. E. DRALEY. Chicago University. U. S. Atomic Energy Comm. Pubn., CT-3043, June 4, 1945 (Declassified January 5, 1956), 20 pp. Available from: Office of Technical Services, Washington, D. C.

Bare uranium slugs 1.4 inches in diameter corrode in distilled water in a steam autoclave at 130 to 150 psi at an average constant rate of 139 mg/cm²/hr based on original area. Steam corrosion of bare uranium slugs, at 130 to 150 psi is roughly the same as in water for about two hours, but is much higher and erratic after that time, measured average values being as high as 1630 mg/cm²/hr. Pinholed, aluminum jacketed slugs corroded in steam at 130 to 150 psi, due to the formation of UH₃ which expanded to pimple the jacket of the slug in every case tested. Uranium binary alloys (including silicon, molybdenum, tantalum, zirconium and niobium) were tested in liquid distilled water under steam pressure of 130 to 150 psi with certain niobium and epsilonized silicon alloys proving resistant to corrosion. (auth)—NSA. 12731

6.3.19, 2.2.2
The Atmospheric Corrosion of Rolled Zinc. E. A. ANDERSON. Paper before Am. Soc. Testing Materials, 58th Ann. Mtg., Symposium on Atmospheric Corrosion of Non-Ferrous Metals, Atlantic City, June 29, 1955. ASTM Special Technical Pubn. No. 175, 1956, 126-134; disc., 134.

Summary of data obtained for three grades rolled zinc exposed to various industrial, marine and rural atmospheres in the ASTM 20-year atmospheric exposure tests. Of the experimental methods used, weight-change determination, after removal of corrosion products, produced most acceptable data. Tension testing of specimens cut from corroded plates has value as a procedure, but methods for correction of aging changes is needed. Discussion of mechanism of atmospheric zinc corrosion shows that frequency of rain and dewfall, acidity of moisture and rate of drying are three factors controlling corrosion. Corrosion rate is at minimum in industrial locations which combine acidic atmospheric contamination with prevalence of heavy mists and dew. Composition of zinc has insignificant bearing on corrosion rate. Tables. —INCO. 12729

6.3.19, 461
Study of Corrosion. Pt. IV. Electrochemical and Corrosion-Kinetic Study of Zinc in Water. (In German.) K. SMRCEK AND K. BARTON. *Collection of Czechoslov. Chem. Communications*, **21**, No. 2, 339-348 (1956) April.

Corrosion behavior in city, industrial, distilled and sea waters at 20 to 95 C. —MR. 12608

6.3.20, 1.4
Zirconium: A Bibliography of Un-

classified **Report Literature.** Technical Information Service Extension. U. S. Atomic Energy Comm., TID-3304, July, 1956, 43 pp. Available from: Office of Technical Services, Washington, D. C.

This bibliography contains 225 annotated references to unclassified reports on zirconium. References are included to reports written prior to September, 1955. Author, subject and report number indexes are provided. (auth) —NSA.
13404

6.3.20, 2.3.4
Effect of Prior Corrosion History on the Corrosion of Zircaloy-2 in High Temperature Water. D. E. THOMAS AND S. KASS. *J. Electrochem. Soc.*, **103**, No. 9, 478-482 (1956) Sept.

A method is presented which permits in a relatively short time the prediction of the corrosion behavior of Zircaloy-2 after long exposure times in high temperature water. The technique, which is

of practical value involves changing the corrosion test temperature and yields transient effects which are of interest from a theoretical point of view. 12610

6.3.20, 3.2.2
Strain-Induced Porosity and Hydrogen Embrittlement in Zirconium. F. FORSCHER. *J. Metals* (Trans. AIME), **8**, Sec. II, 536-543 (1956) May. 13208

6.3.20, 3.2.2, 3.7.4
A Fundamental Investigation of Hydrogen Embrittlement in Zirconium. ARTHUR P. YOUNG AND CHARLES M. SCHWARTZ. Battelle Memorial Inst. U. S. Atomic Energy Comm. Pubn., BMI-1100, June 27, 1956, 24 pp. Available from Office of Technical Services, Washington, D. C.

Investigations were made to determine the relationship between the microstructure and the low impact strength of hydrogenated zirconium. Unnotched tensile samples of degassed zirconium and of hydrogenated zirconium deformed either slowly or at impact velocity were analyzed with light and electron microscopes to determine the relationship between micro-cracks and microstructures. Only few microcracks were observed at the grain boundaries of degassed zirconium while in hydrogenated zirconium, microcracks were more numerous particularly in tensile-impact samples, obviously, formed by parting at interfaces between hydride platelets and zirconium. This may be related to higher incidence of deformation twinning in impact samples. Hydrogen embrittlement in zirconium is, apparently, due to microcrack formation at hydride-zirconium interfaces. Investigation showed some evidence that hydrogen embrittlement decreases with decreasing grain size and is abnormally enhanced by slow prestrain before impact. (auth). —NSA. 13451

6.3.21
Literature Survey on Properties of Bismuth (and Its Alloys). HANS R. STEPHAN. U. S. Atomic Energy Comm. Pubn., NEPA-929, 1949 (Declassified 1956), 48 pp.

Author outlines the occurrence, consumption and general chemical and physical properties of bismuth. Values are given for its d, isotopic composition, melting point, boiling point, vapor pressure, specific heat, coefficient of expansion, thermal conductivity, electrical resistivity, emissivity, modulus of elasticity, Poisson's ratio, hardness, etc. Phase relationships and equilibrium diagrams are presented for alloys with the elements aluminum, carbon, calcium, cadmium, cerium, cobalt, chromium, copper, iron, gallium, mercury, iridium, potassium, lithium, magnesium, manganese, nitrogen, sodium, nickel, phosphorus, lead, palladium, platinum, rhodium, sulfur, antimony, selenium, silicon, tin, titanium and zinc. 11 references. —MA. 13395

6.3.21, 3.8.2
The Anode Behavior of Germanium in Aqueous Solutions. D. R. TURNER. *J. Electrochem. Soc.*, **103**, No. 4, 252-256 (1956) April.

The anode characteristics of η- and ρ-type germanium are different. A large voltage barrier is observed at about 0.8 ma/cm current density at room temperature on η-type but not on ρ-type electrodes. Voltage barrier on 3 ohm-cm η-type germanium anodes breaks down at about 9 volts in many electrolytes. During anodic dissolution the germanium surface appears

to be covered with about a monolayer of oxide or hydroxide. This suggests that germanium goes into solution as a complex ion with the hydroxyl or oxide radicals attached. Mechanism of germanium dissolution suggested by the results of the anode-cathode curves in 0.1N sulfuric acid is shown. Illustrations, 11 references. —INCO. 12629

6.4 Non-Ferrous Metals and Alloys—Light

6.4.4, 3.6.6, 2.2.2, 2.6
Atmospheric Galvanic Corrosion of Magnesium Coupled to Other Metals. H. O. TEEPLE. Paper before ASTM, 58th Ann. Mtg., Symp. on Atmospheric Corrosion of Non-Ferrous Metals, Atlantic City, June 29, 1955. Am. Soc. Testing Materials Special Technical Publication No. 175, 1956, 89-115.

Evaluation of specimens in investigation of atmospheric galvanic corrosion of magnesium coupled to a number of dissimilar metals and alloys (including nickel, Monel and stainless steel). Specimens were exposed at New York, State College, Pa., Kure Beach and Canal Zone, representative of marine, rural, clean marine and marine tropical atmospheres, respectively. Disk-type atmospheric galvanic assemblies used are described. Tabulated summaries of data show average initial weights of anodic and cathodic materials, range of specimen weights, average weight loss of anodic and cathodic materials, final weight range and net weight loss on total time exposure basis. Magnesium used was commercial AZ31B and M1A. Appendix presents disassembly and cleaning procedures for disk couples and sample calculations.—INCO. 12623

6.4.4, 3.8.2
Electrochemical Behavior of Magnesium. Equilibrium Tension-pH Diagrams for Systems Mg/H_2O, Mg/CO_2, $Mg/H_3PO_4/H_2O$ at 25 C. (In French.) J. VAN MUYLDER AND M. POURBAIX. Technical Report No. 39, March, 1956, 29 pp. Centre Belge d'Etude de la Corrosion, 21 rue des Drapiers, Brussels, Belgium.

6.4.4, 3.8.2, 3.6.2
Corrosion Reaction of Magnesium. Rept. X. On the Case that Ions of Metals More Noble than Magnesium Exist in the Aqueous Solution. G. WADA. *J. Chem. Soc. Japan*, Pure Chem. Sec., **77**, No. 5, 762-766 (1956) May.

(1) Corrosion reaction of magnesium in aqueous solutions of potassium chloride containing a small quantity of Cu^{2+} is divided into two steps: the initial step in which Cu^{2+} or Co^{2+} ions are deposited as metal upon magnesium surface and the later one in which, local cells being formed by the deposited metal, electrode reactions occur. The activation energies of both deposition reaction (E_d) and electrode reaction (E_e) are measured by changing the reaction temperature.

(2) E_d's are almost zero and both E_d and E_e decrease by a common coefficient as temperature becomes higher.

(3) This coefficient of decrement is larger in case of Co^{2+} than in case of Cu^{2+}; in the case of Cu^{2+}, it increases with concentration.

(4) Noble metallic ions in the corrosion reagents are not completely deposited on magnesium surface; the greater part are adsorbed on magnesium hydroxide produced as the reaction proceeds. Therefore the properties of local cells are indifferent from the volume of

the reagents when the concentration is kept constant.

(5) The equation representing the activation energies is derived from the electrode reaction velocity and the hydrogen overvoltage on the cathode surface by means of Tafel's equation.—JSPS.
12683

4.4, 4.4.3, 3.4.2
Corrosion Reaction of Magnesium. Rept. IX. On the Solvation to Ions in the Mixed Solvent of Water and Ethanol. G. WADA. *J. Chem. Soc. Japan*, Pure Chem. Sec., **77**, No. 2, 391-395 (1956) Feb.

Using solutions of lithium chloride in a mixed solvent of water and ethanol as corrosion reagents. Activation energies of magnesium corrosion are measured and some physical properties of the reagents are studied. Results are: (1) Activation energy of magnesium corrosion decreases abruptly when the weight fraction of ethanol is above 20%. (2) Heat of solution of lithium chloride in the mixed solvent decreases abruptly over the ethanol concentration of 20%. This is because the water molecules which are hydrated to ions at low concentrations of ethanol are altered by ethanol molecules and both the solvation energy per mole and the number of molecules of solvation are decreased at this concentration. (3) Catalytic action of neutral salts to magnesium corrosion is sure to have a great relationship with the hydrated water molecules to existing ions in the reagents.—JSPS.
12631

6.6 Non-Metallic Materials

6.6.5, 4.6.11, 6.2.3
The Corrosion of Steel in a Reinforced Concrete Bridge. R. F. STRATFULL. *Corrosion*, **13**, No. 3, 173t-178t (1957) March.

Studies were made to determine the cause of accelerated corrosion of reinforcing steel in a concrete bridge in a salt water environment. There was good reason to believe that macro-galvanic corrosion was involved.

Resistivity and corrosion cell ratio charts indicate that the resistivity of concrete decreases as the deterioration of the concrete increases. The lower resistivity measurements of the concrete in the anodic areas indicated that the anodic areas could have been created by the following factors: (1) a greater moisture content in the anodic areas, and (2) a greater sea salt content in the anodic areas.

Cathodic protection may offer a means of curbing corrosion but certain precautions should be taken. All available data indicate that in new installations in salt water environments, corrosion problems can be minimized by using a concrete formulation having minimum porosity and by a design having a maximum coverage of concrete over the reinforcing steel.
13141

6.6.5, 6.2.3
Corroded Reinforcement Destroys Concrete Beams. C. L. SHERMER. Michigan State Univ. *Civil Eng.*, **26**, No. 12, 56-57 (1956) Dec.

Steel reinforcing bars, expanded by oxidation, burst beam concrete exposed to warm moist air in lumber drying kilns. Cracks in concrete progressed most rapidly where shearing stresses were greatest and where there was some slipping due to loss of bond. Protection for reinforcement against corrosion can be provided by use of a good quality

concrete, maintenance of a sufficient distance between steel and exposed concrete surfaces and use of water-proofing applied to concrete. Diagrams; photos.
—INCO.
13359

6.6.6
Properties of Thorium Oxide Ceramics. C. E. CURTIS AND J. R. JOHNSON. Oak Ridge Nat'l. Lab. *J. Am. Ceram. Soc.*, **40**, No. 2, 63-68 (1957) Feb. 1.

Included are data on strength, density, porosity and corrosion resistance of thorium dioxide ceramics formed by dry-pressing and isostatic pressing. Detailed study of densification of thorium dioxide and calcium oxide and theory of this densification mechanism are discussed. Data are presented for corrosion of thorium dioxide in water at 250 C for

50 hours; ceramics were practically unaffected by high temperature water although they were rather porous. Ready dissolution in nitric acid with hydrofluoric acid catalyst was obtained; this is necessary in recovery of U-233 from irradiated thorium dioxide. Tables.—INCO.
13459

6.6.8
Protective Coatings for Polystyrene. J. A. SNYDER, C. F. MARTINO, J. R. WILKINSON AND E. H. WOOD. *Modern Plastics*, **33**, No. 10, 252, 254, 425 (1956) June.

Results show extent of improvement in weathering life that application of a good coating to polystyrene produces. Lack of exceptional weathering properties of polystyrene need not preclude its use in applications where its specific properties are desirable.—BL.
12605

7. EQUIPMENT

7.1 Engines, Bearings and Turbines

7.1

Studies on Ball Bearing Steels. Pt. II. Effect of Some Metallurgical Factors on the Life of Ball Bearing Steels. T. MITSUHASHI, M. UENO AND Y. NAKANO. National Institute of Industrial Technology of Japan, July, 1956, 17 pp.; Translation by W. K. Y. Tao, Science Translation Service, University of Alabama for Bureau of Ships, U. S. Navy: Available from Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (Order PB 121427).

Improvement in the life of Japanese domestic ball bearings was sought through a study of the relationship between metallurgical factors and life-span. Bearing trouble has been occurring mainly at the inner ring, next on the ball and then on the outer race. Using inner rings whose life-span had been determined, tests were run on chemical composition, non-metallic inclusions, hardness, compressive loading, cementite content, grain size and degree of forging. Results showed that chemical composition, nitrogen content and grain size bore no direct relationship to life. Residual cementite after heat treatment had a clear relationship. The life of the bearing was extended as hardness increased after heat treatment. The forging ratio of Japanese ball bearing steels was found to be considerably below that of similar foreign steels. **13265**

7.1

Application of Internal Liquid Cooling to Gas-Turbine Rotors. S. ALPERT, R. E. GREY AND D. D. DRAKE. Paper before Am. Soc. Mech. Engrs., Diamond Jubilee Ann. Mtg., Chicago, November 13-18, 1955. *Trans. ASME*, **78**, No. 6, 1257-1266 (1956) August.

Application of internal liquid cooling to rotor and blades of a gas turbine allows increase in inlet-gas temperature and use of alloys low in strategic materials. Typical alloys selected for different temperature and stress levels were mild steel, AISI 4130, 4340 and 502 steels and chromium-molybdenum-vanadium alloy. Parts subjected to direct impingement of combustion gases were protected by chromizing. Electroless nickel-plating process was used on machined surfaces and silicone-base aluminum paint was applied to sheet metal parts. Cold-air tests, hot tests and endurance tests totaling 100 hours were run on a single-stage test turbine. Aerodynamic and thermodynamic data correlated with expected values and mechanical performance was satisfactory. Illustrations.—INCO. **12667**

7.2 Valves, Pipes and Meters

7.2

Mechanical Seals—Practical Manual. S. ELONKA. *Power*, **100**, No. 3, 109-132 (1956) March.

Detailed report on mechanical seals, their operation, design, classification as stationary vs rotating and balanced vs unbalanced, seal materials with required flatness and surface finish, face combinations and liquids they seal, types and applications of seals available today and methods of cooling seals. Materials listed include bronze, Ni-Resist, nickel cast iron, ceramics, Stellite facing on stainless steel, tungsten-carbide, Teflon, cast iron, 400 series stainless steel, Hastelloys A, B and C, Malcomized Type 316, Monel, aluminum- and phosphorous bronze. Carbon-graphite, ceramics, and ceramic coatings on metal are discussed in detail as important seal face materials. Face combinations are given for water, gasoline, oil, acids, caustics, salt solution and sea water. Tables, diagrams, illustrations.—INCO. **12767**

7.2, 3.6.2

Mechanism of Water Pipe Corrosion. ROLF ELIASSON AND JAMES C. LAMB, II. *Water & Sewage Works* (Reference and Data Ed.), **103**, 99R-104R (1956) June.

Variables affecting rate and distribution of pipeline corrosion. Formation of corrosion cells.—BTR. **12724**

7.2, 4.6.2

Thorex: Valve Test for Steam Service (Taylor No. 1V67804 and Minneapolis-Honeywell No. VO53E). G. A. WEST. Oak Ridge National Lab. U. S. Atomic Energy Comm. Pubn., CF-53-8-173, August 25, 1953 (Declassified February 8, 1956), 9 pp. Available from Office of Technical Services, Washington, D. C.

An evaluation study to determine wear and corrosion in steam service, leakage in steam condensate service, cost comparison, operability of Skinner Electric Solenoid valves and recommendations of remotely operating valves proposed for use in the Thorex pilot plant to throttle steam or water to jets and tank jackets revealed no erosion or excessive wear rings. Leakage tests showed the Taylor valve to be superior and continued operation did not affect leakage in any of the valves tested. Cost recommendations are made.—NSA. **13417**

7.2, 8.4.3, 5.2.1

External Casing Corrosion: Cause, Effect and Control. J. D. SUDBURY. Continental Oil Co. *World Oil*, **144**, No. 1, 163-164, 166, 170 (1957) Jan.

Discusses electrochemical attack due to potential differences and attack due to sulfate reducing bacteria as causes of casing corrosion. Measurement of the electrochemical corrosion, determination of current required for cathodic protection and problems encountered in application of cathodic protection systems are considered. Graphs.—INCO. **13188**

7.3 Pumps, Compressors, Propellers, Impellers

7.3, 8.4.3

What Causes Corrosion in Pumping Wells? P. MENAUL. *World Oil*, **144**, No. 1, 157-159 (1957) Jan.

Explanation of electrolytics, galvanic and chemical mechanisms responsible for corrosion of pumping well components: casing, tubing, rods and pumps. Numerous high resistance connections in pumping well equipment strings make cathodic protection an undesirable protection scheme. Inhibition of hydrogen sulfide corrosion with formaldehyde and cyanimides is discussed.—INCO. **13198**

7.4 Heat Exchangers

7.4.2, 3.2.2

Causes of Fissure Formation in E1257 Steel Pipes of Steam Superheaters. (In Russian.) L. P. TRUSOV, L. P. NIKITINA AND G. A. TULIAKOV. *Metallovedenie i Obrabotka Metallov*, No. 5, 27-33 (1956) May.

Mechanism of fissure formation in pipes of certain types of steam superheaters operating under irregular con-

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ditions. Diagrams, photographs, micrographs, table.—BTR. 　12616

7.4.2, 3.5.3, 3.5.8, 6.3.6
Corrosion, Cracking and Erosion on the Outer Surface of Copper-Alloy Condenser Tubing. Pt. II. (In German.) F. W. NOTHING. *Metall*, **10**, No. 21/22, 1033-1038 (1956) Nov.

Stress corrosion; cracking and corrosion. Corrosion fatigue and erosion.—BTR. 　13336
For Pt. I, see Card No. 12517, classified 7.4.2, 6.3.6, 4.6.2, 4.6.4

7.5 Containers

7.5.2, 5.3.2, 3.6.6, 6.3.14
The Tin-Steel Couple in Air-Free Citric Acid Solution. E. L. KOEHLER. *J. Electrochem. Soc.*, **103**, No. 9, 486-491 (1956) Sept.

In air-free citric acid solution, specimens of uncoupled black plate were found to evolve hydrogen at rates equivalent to the dissolution rates of the steel. Additions of up to 0.3 g SnCl₂·2H₂O/liter progressively decreased corrosion rates. Tin is anodic to and protects steel sacrificially in solutions containing dissolved tin. Hydrogen evolution is decreased by coupling steel to tin not solely by inhibition but also by an apparent shift in the anodic polarization curve of the steel. All observed effects on the corrosion rates in this medium, whether traceable to the steel, dissolved tin inhibitor, or coupling to tin, appear to be the results of variation in anodic properties. 　12765

7.5.2, 8.3.5
Corrosion Mechanisms in the Plain Can. E. L. KOEHLER AND C. M. CANONICO. *Corrosion*, **13**, No. 4, 227t-237t (1957) April.

Quoth Sir Lot of Zinc:

A study was made of the various factors involved in the corrosion of plain tin cans containing fruit products. Results of tests conducted to determine the corrosive effects of prune juice and peaches on tin and steel are reported. Data include such items as amount of hydrogen evolved, amounts of tin and steel dissolved, potential relationships, protective currents and polarization characteristics of coupled tin and steel elements.

The shelf life of a plain tin can containing a fruit product such as prune juice is visualized as being made up of three distinct parts. In the first period the steel base is virtually completely covered with tin and the corrosion process occurring is solution of tin concurrently with reduction of depolarizers in the food product on the tin surface. In the second period, a significant amount of steel base is exposed and the corrosion processes are those of the tin-steel couple. It is significant that in this period not only is the steel base protected by the tin, but the rate of hydrogen evolution per unit area of steel base exposed is markedly reduced by the tin coating. This is not due to the inhibiting effect of dissolved tin but to another mechanism. In the third period, the can is completely detinned and attack is on the steel base alone. The life of the can is largely determined before this period. 　13439

7.5.5, 2.3.4, 5.4.5
Coatings for Crude Oil Tank Bottoms. R. M. CARTER. *Corrosion*, **13**, No. 4, 270t-276t (1957) April.

Corrosion in the bottoms of field-erected tanks handling crude oil continues to be a problem, especially in areas where the oil contains aromatics

or other elements that rapidly deteriorates the hot coal tar coatings generally used. New epoxy resin combinations and other coating innovations have brought forth materials that promise to withstand the more troublesome environments and to compete with the other bottom coatings for general use. However, the array of new brand names, chemical terms, unrelated service claims, etc., can become confusing to the operating man faced with the problem of selecting a protective coating for his particular tank.

This paper describes a method successfully used to screen promising materials in the laboratory. It also discusses field conditions, application problems and other factors that affect the selection and use of successful coatings. 　13443

7.5.5, 8.9.5
Tank Coatings: Clean-Oil Tankers. G. W. COLBERG. Paper before Am. Petroleum Inst., Tanker Corrosion Mtg., Absecon, N. J., June 13-15, 1956. *Marine Eng.*, **61**, No. 8, 53-54, 57; disc., 57 (1956) August.

Account of an oil company's experience with anti-corrosion tank coatings. Coatings considered are vinyls, Epons, metals (particularly zinc) and zinc-pigmented coatings. Surface preparation and application of cathodic protection are mentioned.—INCO. 　12758

7.7 Electrical, Telephone and Radio

7.7
Dust on Relay Contacts. H. J. KEEFER. *Bell Lab. Record*, **35**, No. 1, 25-28 (1957) Jan.

Types of dust encountered, replica technique developed for investigation of failures due to dust and use of dust meters in laboratory tests are discussed. When non-working palladium contacts were operated in tight compartments, number of contact failures increased, due to formation of brown powdery organic polymer formed by reaction of organic vapors on palladium or platinum contacts at time of contact friction.—INCO. 　13190

7.7, 2.2.7, 6.4.2
Aluminum Armor Protects Power Cables: Topic of the Month. D. M. FARNHAM. *Corrosion*, **12**, No. 11, 533t (1956) November.

Metallic armors are placed on underwater power cables to provide mechanical protection to the underlying lead sheath. Although galvanized steel wire is usually used, two years ago 57S aluminum alloy was selected for armoring the power cables crossing the St. Lawrence river, each 35 miles long and having a deep sea portion of 26 miles. The armor is formed of 26 aluminum alloy wires 0.294-inch thick, which, at the shore end, is connected electrically to the lead sheath and grounded. After two years of service the aluminum cable armor showed no signs of corrosion whatsoever.—ALL. 　13207

7.7, 3.5.3
The Erosion of Electrical Contacts by the Normal Arc. W. B. ITTNER AND H. B. ULSH. *Proc. Inst. Elec. Engrs.*, Pt. B, **104**, 63-68 (1957) January.

Measurement of cathode material transfer under action of normal arc for nickel, platinum, palladium, rhodium, irridium, palladium-copper, platinum-iridium (10,

20 and 35 iridium), palladium-ruthenium, platinum - ruthenium, platinum - iridium, platinum-silver, palladium-silver and nickel-palladium-copper-silver electrode materials.—INCO. **13460**

7.7, 5.3.2

The Protection of Cable Sheathing: The Behaviour of Aluminium Sheathed Cables. P. A. RAINE. *Chemistry and Industry*, No. 41, 1102-1111 (1956) Oct. 20. Performance criteria, choice of material, behavior in water and soil, protection against corrosion.—MR. **13320**

7.7 6.3.8, 4.4.3, 3.3.4

The Phenomenon of the So-Called "Phenol Corrosion" of Telephone Cables. (In German.) W. HESS. *Werkstoffe u. Korrosion*, 7, No. 11, 649-652 (1956) November. Concludes that the biological decomposition of the jute and not phenol, is producing the special type of corrosion.—MR. **13252**

7.8 Wires and Cables—Non-Electrical

7.8, 4.6.8, 8.10.3

Corrosion of Haulage Cables and Possible Remedies. (In German.) A. RAUCHE. *Bergbautech.*, 6, 154-157 (1956) March.

Hauling and conveyor ropes of 22-mm diameter used in a copper slate mine showed signs of severe corrosion and had to be replaced after only one third of their expected normal service life. Neither the composition of the mine gases nor the mechanical condition of operation of the ropes could account for the corrosion damage. Although the exterior wires of the ropes, which corroded preferentially, showed a distinct layer of copper, spectroscopic analyses revealed no significant difference between the copper contents of new (0.28% copper) and used (0.26% copper) rope wires.

Exposure of new and used wires for 10 and 45 days to the water dripping down the mine shafts indicated that the mine water was primarily responsible for the corrosion. It contained high amounts of chloride and sulfate ions, as well as of iron, magnesium, calcium, sodium and lithium ions. The original pH of the water was 3.5, but this changed to 7.4 at the point where it touched the rope. Subsequent experiments demonstrated that the tensile strength of wires after 50×10^6 vibrations was 46 kg per sq mm in the dry state; this value was reduced to 3 kg per sq mm, i.e., 8% of the original value, when vibration was carried out in the mine water.—PDA. **13321**

7.10 Other

7.10

Designing Springs for Performance. W. E. FROEHLICH. Associated Spring Corp. *Product Eng.*, 27, No. 9, 135-139 (1956) Sept.

Discusses basic requirements for sound spring design, increased complexity in spring requirements, new spring materials and advances in fabricating techniques. In addition to conventional steel, copper and nickel alloys, current developments are now adding age-hardening non-ferrous alloys (Inconel, Inconel X, S816, and Z nickel); precipitation-hardening stainless steels (17-7PH); nickel alloys with improved corrosion resistance (Ni-Span C); high-strength aluminum

alloys; vacuum-melted steel; phosphate-coated music wire; and some non-metallic materials.—INCO. **13212**

8. INDUSTRIES

8.2 Group 2

8.2.2, 3.1, 5.1

Corrosion. H. P. Kallen. *Power*, 100, No. 12, 73-108 (1956) Dec.

Discusses electrochemical theory of corrosion, various types and forms of corrosion encountered, cathodic protection, modern engineering materials and their selection, inert barriers of organic, metallic or vitreous materials, taming of corrodent by eliminating dissolved oxygen and reducing carbon dioxide, humidity control, use of inhibitors and temporary protection during shipment and storage. With specific reference to corrosion problems in power field, corrosion in steam and condensate systems, cooling system and refrigeration system corrosion, high and low temperature corrosion problems presented by combustion, machinery and structure corrosion and underground corrosion are considered. Laboratory, plant and field tests include mechanical, chemical and electrochemical and electrical methods. Numerous charts, diagrams and photographs.—INCO. **13257**

8.4 Group 4

8.4.3, 5.8.2

Corrosion Measurements in a Hydrogen Sulfide-Water Absorption Pilot Plant. B. W. BRADLEY AND N. R. DUNNE.

Corrosion, 13, No. 4, 238t-242t (1957) April.

In evaluating gas processing facilities to sweeten an extremely sour natural gas, technologists estimated high pressure water absorption followed by simple low pressure flashing would be attractive. Consideration of reduced heat exchange and stripping heat requirements indicated that appreciable savings in investment and operating costs could be effected by the process. Accordingly, a water absorption pilot plant was constructed and operated for a brief period to establish the absorption and desorption characteristics under the existing field conditions. Since corrosion problems were anticipated, a series of corrosion evaluation tests were conducted concurrently in the pilot plant.

Carbon steel corrosion rates, although very high during the first few hours or days, were found to diminish to a tolerable level within the 19-day test. Killed carbon steel, stainless steel Type 304, Inconel and K-Monel, were found resistant to sulfide stress corrosion cracking. Inconel, Monel, and 304 also showed low weight loss corrosion. Hydrogen probes indicated decreasing corrosion rates in absorber and degasifying drums during the test period. A water dispersable, amine type inhibitor reduced carbon steel corrosion rates and indicated protection from sulfide stress corrosion cracking.

Data indicated stress relieved carbon steel vessels and piping with corrosion resistant alloys for critical process parts, such as pumps, Bourdon tubes, thermometer wells, orifice plates and relief valve springs would provide acceptable service life. The test data also indicate

carbon steel weight loss and sulfide corrosion cracking severity of the environment can be reduced by inhibition. 13433

8.4.5
Process Engineering at the Hanford Separation Plants. CHARLES A. ROHRMANN. Hanford Atomic Products Operation. *Nucleonics*, 14, No. 6, 66-68 (1956) June.

Plants for the separation of uranium, plutonium and fission products from spent reactor fuel by continuous solvent extraction processes and the problems that must be solved in remotely controlled, radioactive corrosive systems are discussed. —NSA.   13356

8.4.5
Corrosion Problems in Nuclear Reactor Power Stations. W. Z. FRIEND. Paper before Am. Power Conf., 18th Ann. Mtg., Chicago, March 21-23, 1956. *Proc. Am. Power Conf.*, **18**, 613-628 (1956).

Discussion of corrosion of construction materials used in nuclear power plants in which water is used both as primary coolant and for steam generation. Metallic materials used in atomic reactors are classified as fuel element or construction materials. Fuel element materials include solid fuels and fuel-cladding. Cladding materials most frequently used to date are aluminum and zirconium alloys and stainless steel and beryllium cladding. Crevice and stress corrosion cracking in reactors are discussed. Nuclear radiation under high flux density has a significant effect on mechanical and physical properties of metals and alloys which affect corrosion resistance. Corrosion of stainless steels, nickel, Inconel, Monel, copper-nickel alloys and Hastelloys in high purity water is discussed. Tables, graphs, 18 references.—INCO.   13201

8.4.5
Field Corrosion Tests in Purex Acid, Uranium and Waste Concentrators. N. D. GROVES AND K. M. HAWS. Hanford Atomic Products Operation, Richland, Washington. U. S. Atomic Energy Comm. Pubn., HW-42884, June 28, 1956, 10 pp. Available from: Office of Technical Services, Washington, D. C.

A program for field corrosion tests in Purex acid, uranium and waste concentrators using small heat exchangers is presented.—NSA.   13228

8.4.5
The Use of Water in Atomic Reactors. H. W. HUNTLEY AND S. UNTERMEYER. Paper before Am. Soc. Testing Materials Symp. on High-Purity Water Corrosion, Atlantic City, June 28, 1955. ASTM Special Technical Publication No. 179, 1956, 8-18.

Describes the water requiremnets of various parts of reactor cooling systems for reactors used in power sources as well as for non-power applications. Possible sources of radioactivity present in primary water system are: activation of oxygen in water molecule; activation of impurities in water which results from corrosion of reactor, other components in system and in leakage of condenser cooling water; and failure of nuclear fuel cladding. An example of application of a purification system to a specific power plant is given in order to estimate radioactivity in a turbine. Tables, flow sheets.—INCO.   13175

8.4.5
Materials for Nuclear Power Reactors. J. M. WARDE. *Materials & Methods*, 44, No. 2, 121-144 (1956) August.

Structural materials used within reactor must be selected on basis of low neutron absorption characteristics and physical and chemical properties. Materials of major interest are stainless steels, aluminum, zirconium and nickel base alloys. Austenitic stainless steels have a wide variety of applications in reactor service because of general good corrosion properties and high temperature performance. Stabilized classes such as AISI 321 or 347 are of special interest because of their resistance to intergranular corrosion. Inconel X, Nimonic 80 and 90 can be used for reactor plumbing, heat exchanger fabrication and other reactor auxiliaries. Advantages of alloys include excellent corrosion resistance and good mechanical strength but chief disadvantage is relatively high thermal neutron capture cross-section. Illustrations.—INCO.   12675

8.4.5, 4.3.3
Dynamic Slurry Corrosion Studies (for) Quarter Ending January 31, 1956. E. L. COMPERE, H. C. SAVAGE, S. A. REED, G. E. MOORE, R. M. WARNER, R. M. PIERCE AND S. R. BUXTON. Oak Ridge National Lab. U. S. Atomic Energy Comm. Pubn., CF-56-1-168, March 27, 1956, 41 pp. Available from: Office of Technical Services, Washington, D. C.

Corrosion data are presented for three slurry runs at 300 C on the 100A pump loop using three different preparations of thorium dioxide. Average circulating concentrations ranged from 581 to 1075 g thorium/kg water. Operating problems including some caking and plugging are discussed. One water run was also

made. The attack rate by slurries in the pump loop on pin specimens of Type 347 stainless steel appears to be proportional to the slurry concentration and to the square of the flow velocity. Platinum, gold, Zircaloy-2 and titanium appear to be attacked relatively less severely than stainless steel, which had a pin corrosion rate of 7 mil/year at 20 ft³/sec and 100 g thorium/kg water. Studies at 250 C in toroids found no effect of increased thorium dioxide calcination temperature on the attack rate on Type 347 stainless steel, titanium or Zircaloy-2 at various flow velocities.—NSA. 12739

8.8 Group 8

8.8.1, 4.3.2
Solving Unexpected Corrosion Problems. G. D. GARDNER. National Petro-

chemical Corp. *Chem. Eng.,* **64,** No. 2, 292, 294, 296, 298, 300 (1957) Feb.

Although hydrocarbon feed stocks and all end-products are non-corrosive, most of problems developed because of acids (sulfuric acid and hydrochloric acid) required for chemical reactions, with most serious corrosion problems occurring in units producing ethyl alcohol. When carbon steel piping carrying cold concentrated sulfuric acid plugged up with sodium salts, high velocities of steam used to melt plugging also removed protective ferrous sulfate layer, rapidly thinning elbows. Solution was increase in pipe size to reduce steam velocity. Duriron Y was used for gate valves in handling 45% sulfuric acid after Hastelloy B exhibited galvanic corrosion when coupled with carbon and graphite; table shows effect of carbon on corrosion of Hastelloy B in 45% sulfuric acid (C.P. and sludge). Copper tubing of

surface condenser handling 5% sulfuric acid vapor showed erosion-corrosion; acidic vapors impinged on inside of tubes; erosion was reduced by substituting hard aluminum-bronze alloy (Ampco 8). Copper and Monel piping carrying hot hydrocarbon vapors with up to 9% sulfur dioxide failed; Type 316 was substituted. Tables include corrosion data for Type 316, Aloyco 20 and 35, Hastelloy B and D, chemical lead, Inco 803 copper, various bronzes, Nionel and Monel.—INCO. 1347.

8.8.1, 4.3.5
Materials for Fluorine Generator Anode Assemblies. R. E. SIMMONS, W. R. ROSS, MASSLER, C. W. HOSKINS AND R. A. JOHNSTON. Union Carbide Nuclear Co., Paducah Plant, U. S. Atomic Energy Comm. Pubn., KY-191, Sept. 28, 1956, 13 pp. Available from Office of Technical Services, Washington, D. C.

Corrosion of anode assembly materials in fluorine generators is pronounced, therefore, selection of the proper materials of construction is important. Several metals and alloys have been tested for corrosion resistance when anodic in a fluorine test cell. The relative corrosion resistance of most of the materials has been determined by three methods. The current-voltage method is the most rapid and, generally, is verified by the other two methods. By this method, current-voltage curves are obtained for the material under test. The corrosion is proportional to the current, therefore, the relative corrosion rate as a function of the voltage may be obtained by referring to the curve. In general, copper, copper alloys and magnesium alloys offer the best corrosion resistance. The resistance of copper is improved by alloying with zinc, phosphorus, tin, beryllium and aluminum, but lead and silicon have the opposite effect. The resistance of mild steel is little changed by addition of alloying elements. High nickel alloys, lead, aluminum and cast iron were severely corroded. Several materials which offer good corrosion resistance at low voltages (i.e. 10 volts) were badly pitted at voltages above the breakdown voltage. (auth)—NSA. 13353

8.8.3, 5.4.8, 2.2.5
Plastisols: Tough Protective Coatings for Plating Equipment. D. R. MESERVE. *Plating,* **43,** No. 10, 1244-1247 (1956) October.

Alkali and acid resistant, long-lasting vinyl plastic coatings applied to plating equipment by dipping or spraying (thickness 0.0025 to 0.25-inch in one application). Series of exacting exposure tests under plating conditions.—BNF. 13278

8.8.5, 7.6.9
Electric Heat Treatment Furnaces. J. B. CARROLL. *Elec. Review,* **160,** 71-75 (1957) Jan. 11.

Review of current designs and applications of electric heat-treatment furnaces covering: elements made of nickel-chromium or nickel-chromium-iron alloys; corrosion problems; shielding of elements by refractories in carburizing atmosphere; nickel-aluminum-chromium alloy developed for operation up to 1200/1250 C; and Kanthal for use up to 1350 C. Batch furnaces, bright hardening or carbonitriding process; malleabilizing of cast iron, gas carburizing, brazing furnace used for annealing and fluxless brazing of stainless steel and Nimonic alloys and continuous furnaces are discussed. Illustrations of Birlec furnaces are given.—INCO. 13462

INDEX TO ADVERTISERS

8.9 Group 9

8.9.1

High-Speed Problems of Large Airplanes. G. S. SCHAIRER. Paper before Am. Soc. Mechanical Engrs., Aviation Conf., Los Angeles, March 14-16, 1956. *Mech. Eng.,* **78,** No. 9, 832-836 (1956) Sept.

Discussion of new concepts in aerodynamic design, structure and material that must be evolved for successful operation at high Mach numbers and high temperature. Graph of tensile strength of corrosion-resistant steel, titanium, aluminum and magnesium versus temperature shows that aluminum and magnesium deteriorate at about Mach 2 but titanium and steel retain most of their strength at temperatures encountered up to Mach 3. Efficiencies of structural panels in compression at 60 and 500 F are given for 17-7 PH sheet and sandwich and 6Al-4V titanium sheet and sandwich. Graphs.—INCO.   13347

8.9.1, 7.1

Stainless Steels and High-Temperature Materials in Aeronautics. L. GUITTON. *Metaux: Corrosion-Industries,* **31,** 407-417 (1956) October.

Review of service requirements involved in gas-turbine components. Development of high-temperature resistant materials based on modified 80/20 iron-containing nickel-chromium alloys includes French, American and British work. Evolution of the Nimonic series is traced.

Notes on materials used in construction of Nene and Tay jets produced by Hispano-Suiza, Atar jet by SNECMA and in Turbomeca jets are included. Mention is made of RR. 102 (22 chromium-14 nickel), QA 18 or Nicral Z or ATGS (equivalents of Nimonic 75), Nicral T or NS 190 (an 18/10 chromium-nickel steel + 4 tungsten), ATVS-7 (a nickel-chromium-cobalt alloy containing 34 iron), NS 20 C (equivalent to Type 321), NS 24 (equivalent to Type 309) and NS 30 or Nicral D (equivalent to Type 310).—INCO.   13225

8.9.3, 5.4.5

How Pipe Coatings Affect Complete Protection Programs. A. S. JOY. *Petroleum Engr.,* **28,** No. 3, D22-D25 (1956); *Chem. Absts.,* **50,** No. 11, 8226g (1956).

A review of pipe coating methods, materials and results. 17 references.—RPI.   13458

8.9.5, 5.2.1

Cathodic Protection for Small Shipping. M. G. DUFF AND I. D. G. GRAHAM. *Corrosion Technology,* **4,** No. 1, 9-12 (1957) Jan.

Deals with cathodic protection requirements of small vessels—coastal shipping, fishing vessels, tugs, lighters and yachts. Development of anodes and their service on steel and wooden vessels are discussed. Bulk factor of anodes is a problem considered.—INCO.   13466

32 **DURIRON® ANODES** protect 11,000 feet
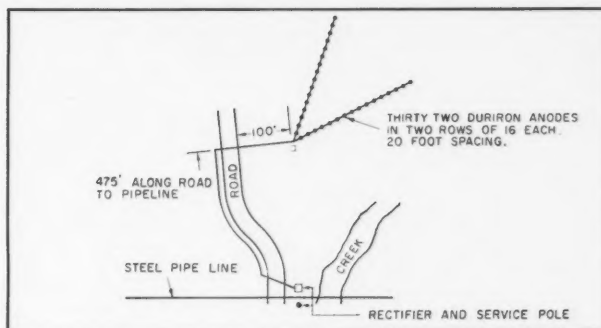# of steel water line without backfill

The Problem:

An isolated section of 11,000 feet of steel water line needed cathodic protection. Tests showed current requirements to be 40 amps., but replacement of adjacent wood stave lines called for extra capacity. Ground was a peat bog with water table standing at 6 inches below surface, making backfill methods impossible.

The Installation:
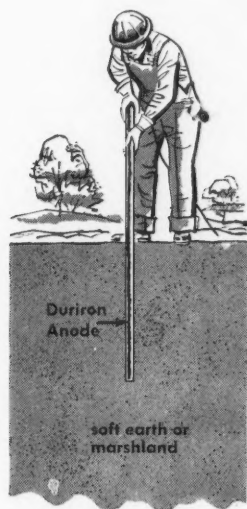
32 Duriron Anodes (2″ x 60″) were installed without backfill, by digging through the dry surface and then pushing anodes down until the tops were 3 feet below surface. Anodes were installed 20 feet apart, in two rows, with a calculated resistance of one ohm, based on previous experience with similar installations. While conventional backfill columns would have reduced the number of anodes necessary, the use of bare anodes constituted a major saving in cost.

Duriron Anode

soft earth or marshland

THIRTY TWO DURIRON ANODES IN TWO ROWS OF 16 EACH. 20 FOOT SPACING.

—100'—

475' ALONG ROAD TO PIPELINE

ROAD

CREEK

STEEL PIPE LINE

RECTIFIER AND SERVICE POLE
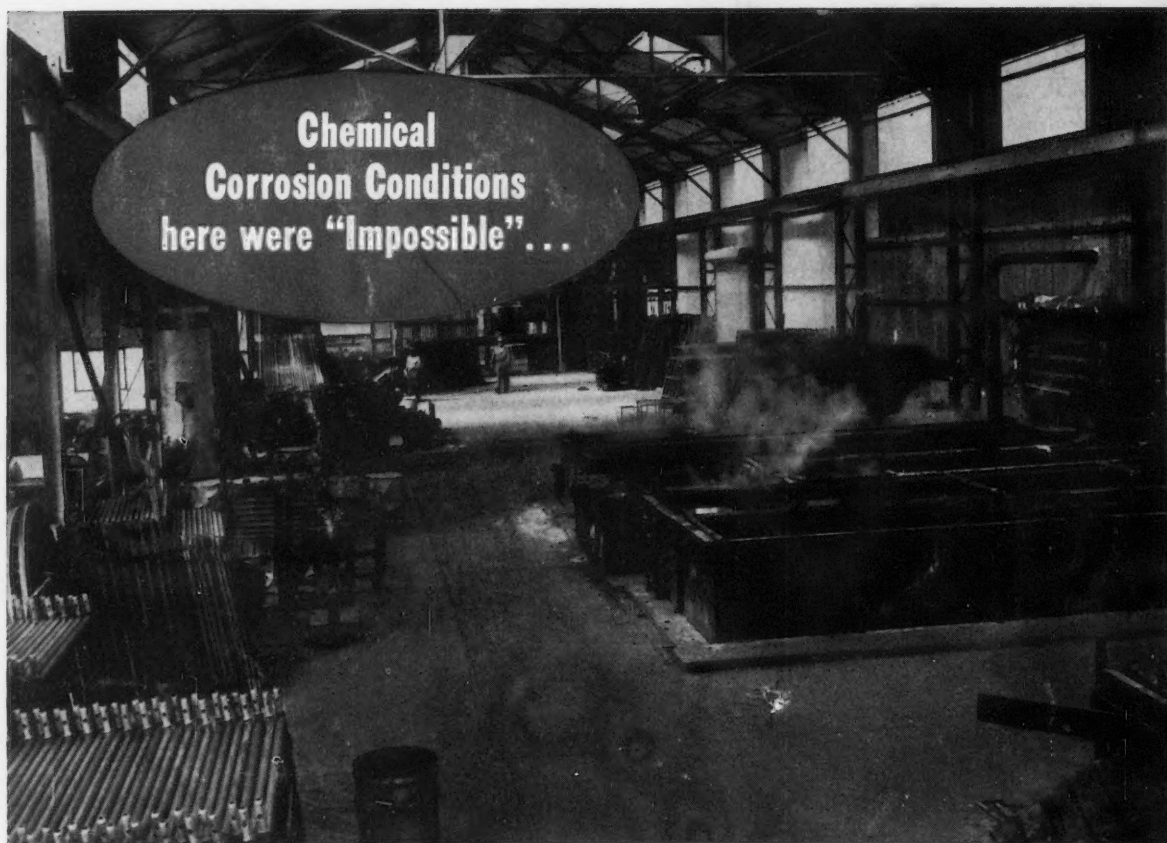
The Performance:

The anode bed is discharging 60 amps. at a terminal voltage of 59 volts. The entire line section is under protection, the minimum potential being 1.18 volts. This affords ample margin to handle prospective additions to the line. Agreement between actual and calculated anode resistance is quite close.

Action:

For further information on this particular installation or for technical assistance on other Duriron impressed current anode installations, write:
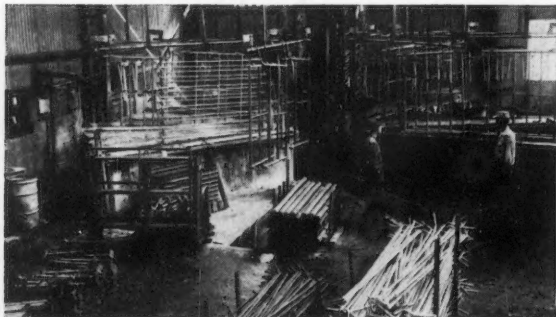
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If you have a stubborn corrosion problem that you've labeled as economically "impossible" to control, it will pay you to investigate *Tarset*. Send today for complete technical data and samples for testing.

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